

THE UNITED STATES PATENT AND TRADEMARK OFFICE

U.S. Pat. No.:	7,572,301	§
		§
Application No.:	10/592,976	§
		§
Issue Date:	August 11, 2009	§
		§
Inventor(s):	Athanassios Tziaks et al.	§
		§

Certificate of Corrections Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

REQUEST FOR CERTIFICATE OF CORRECTION

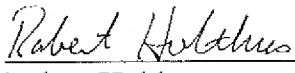
Dear Sir:

Pursuant to 37 C.F.R. § 1.322, Applicants request an expedited issuance of a Certificate of Correction for the above-identified patent which has been assigned to Huntsman International LLC. Applicants submit herewith the text of the correction requested on Certificate of Correction Form PTO/SB/44 which illustrates the second ring of the dye of formula (2) drawn in broken lines. Applicants further submit evidence demonstrating the mistake was attributable solely to the Office.

Applicants believe no fee is due for this Request. However, should any fee be due, the Commissioner for Patents is hereby authorized to deduct said fee from Huntsman Corporation Deposit Account No. 08-3442.

Respectfully Submitted,

Huntsman International LLC
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Date: 12/28/11

Encl: - Form PTO/SB/44
- Copy of International Application as filed
- Preliminary Amendment filed 09/15/2006
- Response to Office Communication filed 03/16/2009
- Notice of Allowance mailed 04/06/2009
- Copy of U.S. Pat. No. 7,572,301

UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

Page 1 of 1

PATENT NO. : 7,572,301

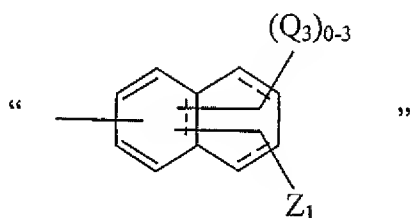
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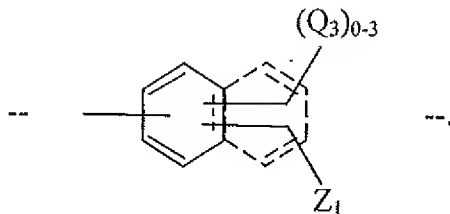
INVENTOR(S) : Athanassios Tzikas; Georg Roentgen; Hubert Jean Luc Christnacher

It is certified that an error appears or errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Abstract and in column 1, lines 53-58, column 50, lines 60-65 and column 55, lines 3-8, the radical of formula (2) appearing as



in each occurrence should appear as



MAILING ADDRESS OF SENDER (Please do not use customer number below):

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This collection of information is required by 37 CFR 1.322, 1.323, and 1.324. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1.0 hour to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Attention Certificate of Corrections Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
29 September 2005 (29.09.2005)

PCT

(10) International Publication Number
WO 2005/090484 A1

(51) International Patent Classification⁷: C09B 62/09, 62/513, 62/475

(21) International Application Number:
PCT/EP2005/051044

(22) International Filing Date: 9 March 2005 (09.03.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
04101144.6 19 March 2004 (19.03.2004) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

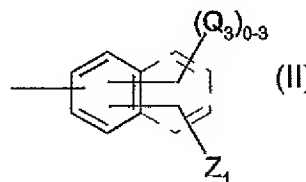
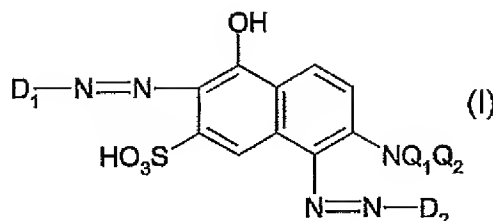
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FIBRE-REACTIVE DYES, THEIR PREPARATION AND THEIR USE



(57) Abstract: Reactive dyes of formula (I), wherein Q₁ and Q₂ are each independently of the other hydrogen or unsubstituted or substituted C₁-C₄alkyl, D₁ is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye, D₂ has the same definition as D₁ or is a radical of formula (II), wherein (Q₃)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄alkyl, C₁-C₄alkoxy, carboxy and sulfo and Z₁ is a radical of formula -SO₂-Y (3a), -NH-CO-(CH₂)_m-SO₂-Y (3b), -CONH-(CH₂)_n-SO₂-Y (3c), -NH-CO-CH(Hal)-CH₂-Hal (3d) or -NH-CO-C(Hal)=CH₂ (3e), Y is vinyl or a -CH₂-CH₂-U radical and U is a group that is removable under alkaline conditions, m and n are each independently of the other the number 2, 3 or 4, and Hal is halogen, are suitable for dyeing cellulosic or amide-group-containing fibre materials.

Fibre-reactive dyes, their preparation and their use

The present invention relates to fibre-reactive dyes, to a process for their preparation and to their use in the dyeing or printing of textile fibre materials.

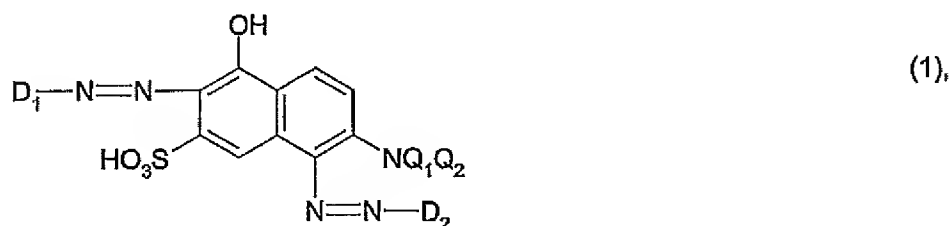
The practice of dyeing using reactive dyes has recently led to higher demands being made on the quality of the dyeings and the economic efficiency of the dyeing process. As a result, there continues to be a need for novel reactive dyes having improved properties, especially in respect of their application.

Dyeing nowadays requires reactive dyes that have sufficient substantivity and at the same time have good ease of washing off of unfixed dye. They should also have a good colour yield and high reactivity, the objective being to provide especially dyeings having high degrees of fixing. The known dyes do not satisfy these requirements in all properties.

The problem underlying the present invention is accordingly to find, for the dyeing and printing of fibre materials, novel improved reactive dyes having the qualities characterised above to a high degree. The novel dyes should especially be distinguished by high fixing yields and high fibre-dye bond stabilities, and in addition it should be possible for dye not fixed to the fibre to be washed off readily. The dyes should also yield dyeings having good allround fastness properties, for example fastness to light and to wetting.

It has been found that the problem posed is largely solved by the novel dyes defined hereinbelow.

The present invention therefore relates to reactive dyes of formula



wherein

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Q_1 and Q_2 are each independently of the other hydrogen or unsubstituted or substituted C_1 - C_4 alkyl,

D_1 is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye,

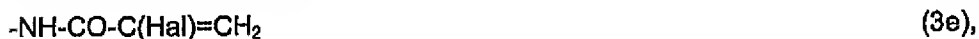
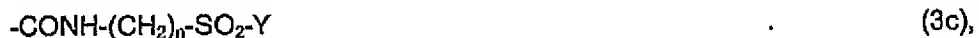
D_2 has the same definition as D_1 or is a radical of formula



wherein

$(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, carboxy and sulfo and

Z_1 is a radical of formula



Y is vinyl or a $-\text{CH}_2\text{-CH}_2\text{-U}$ radical and U is a group that is removable under alkaline conditions,

m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen,

with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

As C_1 - C_4 alkyl there come into consideration for Q_1 , Q_2 and Q_3 , each independently of the others, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and tert-butyl, especially methyl and ethyl. The alkyl radicals Q_1 and Q_2 may be unsubstituted or may be substituted, for example, by hydroxy, sulfo, sulfato, cyano, carboxy, C_1 - C_4 alkoxy or by phenyl, preferably by hydroxy, sulfo, C_1 - C_4 alkoxy or by phenyl. The corresponding unsubstituted radicals are preferred.

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Preferably, one of the radicals Q_1 and Q_2 is hydrogen and the other of the radicals Q_1 and Q_2 is one of the above-mentioned unsubstituted or substituted C_1 - C_4 alkyl radicals.

Q_1 and Q_2 are especially preferably hydrogen.

As C_1 - C_4 alkoxy there come into consideration for Q_3 , for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy and tert-butoxy, preferably methoxy and ethoxy and especially methoxy.

As halogen there come into consideration for Q_3 , for example, fluorine, chlorine, bromine and iodine, preferably chlorine and bromine and especially chlorine.

Preferably, $(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy and sulfo, especially methyl, methoxy and sulfo.

Hal is, for example, chlorine or bromine, especially bromine.

As leaving group U there come into consideration, for example, -Cl, -Br, -F, -OSO₃H, -SSO₃H, -OCO-CH₃, -OPO₃H₂, -OCO-C₆H₅, -OSO₂- C_1 - C_4 alkyl and -OSO₂-N(C_1 - C_4 alkyl)₂. U is preferably a group of formula -Cl, -OSO₃H, -SSO₃H, -OCO-CH₃, -OCO-C₆H₅ or -OPO₃H₂, especially -Cl or -OSO₃H and more especially -OSO₃H.

Examples of suitable radicals Y are accordingly vinyl, β -bromo- or β -chloro-ethyl, β -acetoxy-ethyl, β -benzoyloxyethyl, β -phosphatoethyl, β -sulfatoethyl and β -thiosulfatoethyl.

Preferably, Y is independently vinyl, β -chloroethyl or β -sulfatoethyl, especially vinyl or β -sulfatoethyl.

m and n are preferably each independently of the other the number 2 or 3.

m is especially preferably the number 3.

n is especially preferably the number 2.

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Preferably, Z_1 is a radical of formula (3a), (3b) or (3c), especially of formula (3a) or (3c) and more especially of formula (3a), the variables having the definitions and preferred meanings given hereinabove.

As substituents of the radical D_1 there come into consideration the substituents customary for azo dyes. The examples which follow may be mentioned: C_1 - C_4 alkyl, which is understood to include methyl, ethyl, n- and iso-propyl and n-, iso-, sec- and tert-butyl; C_1 - C_4 alkoxy, which is understood to include methoxy, ethoxy, n- and iso-propoxy and n-, iso-, sec- and tert-butoxy; hydroxy- C_1 - C_4 alkoxy; phenoxy; C_2 - C_6 alkanoylamino unsubstituted or substituted in the alkyl moiety by hydroxy or by C_1 - C_4 alkoxy, such as, for example, acetylamino, hydroxyacetyl-amino, methoxyacetylamino or propionylamino; benzoylamino unsubstituted or substituted in the phenyl moiety by hydroxy, sulfo, halogen, C_1 - C_4 alkyl or by C_1 - C_4 alkoxy; C_1 - C_8 alkoxy-carbonylamino unsubstituted or substituted in the alkyl moiety by hydroxy, C_1 - C_4 alkyl or by C_1 - C_4 alkoxy; phenoxycarbonylamino unsubstituted or substituted in the phenyl moiety by hydroxy, C_1 - C_4 alkyl or by C_1 - C_4 alkoxy; amino; N- C_1 - C_4 alkyl- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, C_1 - C_4 alkoxy, carboxy, cyano, halogen, sulfo, sulfato, phenyl or by sulfophenyl, such as, for example, methylamino, ethylamino, N,N-dimethylamino, N,N-diethylamino, β -cyanoethylamino, β -hydroxyethyl-amino, N,N-di- β -hydroxyethylamino, β -sulfoethylamino, γ -sulfo-n-propylamino, β -sulfato-ethylamino, N-ethyl-N-(3-sulfobenzyl)-amino, N-(β -sulfoethyl)-N-benzylamino; cyclohexyl-amino; N-phenylamino or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted in the phenyl moiety by nitro, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, carboxy, halogen or by sulfo; C_1 - C_4 -alkoxycarbonyl, for example methoxy- or ethoxy-carbonyl; trifluoromethyl; nitro; cyano; halogen, which is generally understood to include, for example, fluorine, bromine and especially chlorine; ureido; hydroxy; carboxy; sulfo; sulfomethyl; carbamoyl; carbamido; sulfamoyl; N-phenylsulfamoyl or N- C_1 - C_4 alkyl-N-phenylsulfamoyl unsubstituted or substituted in the phenyl moiety by sulfo or by carboxy; methyl- or ethyl-sulfonyl; and C_1 - C_4 alkyl-sulfonylamino.

Fibre-reactive radicals are also suitable as substituents of the radical D_1 .

Fibre-reactive radicals, such as, for example, the above-mentioned radicals of formulae (3a) to (3e), are to be understood as being those which are capable of reacting with the hydroxy

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groups of cellulose, with the amino, carboxy, hydroxy and thiol groups in wool and silk or with the amino groups and, possibly, with the carboxy groups of synthetic polyamides, to form covalent chemical bonds. The fibre-reactive radicals are generally bonded to the dye radical directly or by way of a bridging member. Suitable fibre-reactive radicals are, for example, those which contain at least one removable substituent at an aliphatic, aromatic or heterocyclic radical or in which the said radicals contain a radical suitable for reaction with the fibre material, for example a vinyl radical.

A fibre-reactive radical present in D_1 corresponds, for example, to the above formula (3a), (3b), (3c), (3d) or (3e) or to the formula



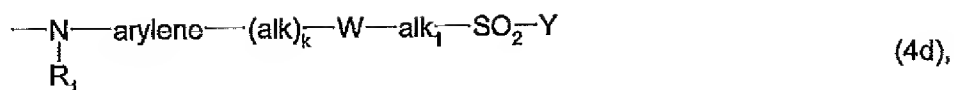
wherein

X_1 is halogen, 3-carboxypyridin-1-yl or 3-carbamoylpyridin-1-yl,

T_1 independently has the same definition as X_1 , is a non-fibre-reactive substituent or is a fibre-reactive radical of formula



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wherein

R₁, R_{1a} and R_{1b} are each independently of the others hydrogen or C₁-C₄alkyl,

R₂ is hydrogen, C₁-C₄alkyl unsubstituted or substituted by hydroxy, sulfo, sulfato, carboxy or

by cyano, or a radical $\begin{array}{c} \text{R}_3 \\ | \\ \text{---alk---SO}_2 \text{---Y} \end{array}$

R₃ is hydrogen, hydroxy, sulfo, sulfato, carboxy, cyano, halogen, C₁-C₄alkoxycarbonyl, C₁-C₄alkanoyloxy, carbamoyl or the group -SO₂-Y,

alk and alk₁ are each independently of the other linear or branched C₁-C₈alkylene,

arylene is a phenylene or naphthylene radical unsubstituted or substituted by sulfo, carboxy, C₁-C₄alkyl, C₁-C₄alkoxy or by halogen,

Q is an -O- or -NR₁- radical wherein R₁ is as defined above,

W is a -SO₂-NR₂-, -CONR₂- or -NR₂CO- group, wherein R₂ is as defined above,

Y has the definition and preferred meanings given hereinabove,

Y₁ is a -CH(Hal)-CH₂-Hal or -C(Hal)=CH₂ group and Hal has the definition and preferred meanings given hereinabove,

k is the number 0 or 1,

X₂ is halogen or C₁-C₄alkylsulfonyl,

X₃ is halogen or C₁-C₄alkyl and

T₂ is hydrogen, cyano or halogen.

R₁, R_{1a} and R_{1b} are each independently of the others preferably hydrogen, methyl or ethyl and especially hydrogen.

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R₂ is preferably hydrogen or C₁-C₄alkyl, such as, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl and especially hydrogen, methyl or ethyl. Especially preferably, R₂ is hydrogen.

R₃ is preferably hydrogen.

When T₁ is a non-fibre-reactive substituent it may be, for example, hydroxy; C₁-C₄alkoxy; C₁-C₄alkylthio unsubstituted or substituted, for example, by hydroxy, carboxy or by sulfo; amino; amino mono- or di-substituted by C₁-C₈alkyl, wherein the alkyl may itself be substituted, for example, by sulfo, sulfato, hydroxy, carboxy or by phenyl, especially by sulfo or by hydroxy, and may be interrupted one or more times by the radical -O-; cyclohexylamino; morpholino; N-C₁-C₄alkyl-N-phenylamino, phenylamino or naphthylamino, wherein the phenyl or naphthyl is unsubstituted or substituted, for example, by C₁-C₄alkyl, C₁-C₄alkoxy, C₂-C₄alkanoylamino, carboxy, sulfo or by halogen and the alkyl is unsubstituted or substituted, for example, by hydroxy, sulfo or by sulfato.

Examples of suitable non-fibre-reactive substituents T₁ are amino, methylamino, ethylamino, β-hydroxyethylamino, N-methyl-N-β-hydroxyethylamino, N-ethyl-N-β-hydroxyethylamino, N,N-di-β-hydroxyethylamino, β-sulfoethylamino, cyclohexylamino, morpholino, 2-, 3- or 4-chlorophenylamino, 2-, 3- or 4-methylphenylamino, 2-, 3- or 4-methoxyphenylamino, 2-, 3- or 4-sulfophenylamino, 2,5-disulfophenylamino, 2-, 3- or 4-carboxyphenylamino, 1- or 2-naphthylamino, 1-sulfo-2-naphthylamino, 4,8-disulfo-2-naphthylamino, N-ethyl-N-phenylamino, N-methyl-N-phenylamino, methoxy, ethoxy, n- or iso-propoxy and hydroxy.

As a non-fibre-reactive substituent, T₁ is preferably C₁-C₄alkoxy; C₁-C₄alkylthio unsubstituted or substituted by hydroxy, carboxy or by sulfo; hydroxy; amino; N-mono- or N,N-di-C₁-C₄alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N-C₁-C₄alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring in the same way as phenylamino and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups.

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Especially preferred non-fibre-reactive substituents T_1 are amino, N-methylamino, N-ethylamino, N- β -hydroxyethylamino, N-methyl-N- β -hydroxyethylamino, N-ethyl-N- β -hydroxyethylamino, N,N-di- β -hydroxyethylamino, β -sulfoethylamino, morpholino, 2-, 3- or 4-carboxyphenylamino, 2-, 3- or 4-sulfophenylamino, 2,5-disulfophenylamino and N-C₁-C₄-alkyl-N-phenylamino.

X_1 is preferably halogen, for example fluorine, chlorine or bromine and especially preferably chlorine or fluorine.

T_2 , X_2 and X_3 as halogen are, for example, fluorine, chlorine or bromine, especially chlorine or fluorine.

X_2 as C₁-C₄alkylsulfonyl is, for example, ethylsulfonyl or methylsulfonyl and especially methylsulfonyl.

X_3 as C₁-C₄alkyl is, for example, methyl, ethyl, n- or iso-propyl or n-, iso- or tert-butyl and especially methyl.

X_2 and X_3 are preferably each independently of the other chlorine or fluorine.

T_2 is preferably cyano or chlorine.

alk and alk₁ are each independently of the other, for example, a methylene, ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene or 1,6-hexylene radical or a branched isomer thereof.

Preferably, alk and alk₁ are each independently of the other a C₁-C₄alkylene radical and especially preferably an ethylene radical or propylene radical.

arylene is preferably an unsubstituted or, for example, sulfo-, methyl-, methoxy- or carboxy-substituted 1,3- or 1,4-phenylene radical, and especially preferably an unsubstituted 1,3- or 1,4-phenylene radical.

Q is preferably -NH- or -O- and especially preferably -O-.

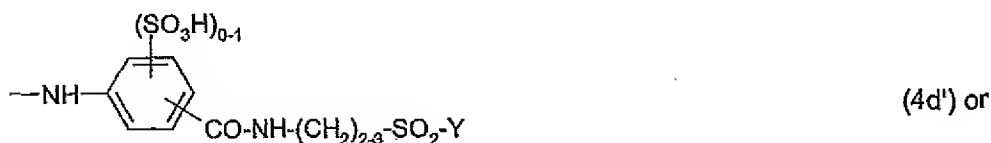
- 9 -

W is preferably a group of formula -CONH- or -NHCO-, especially a group of formula -CONH-.

k is preferably the number 0.

The reactive radicals of formulae (4a) to (4f) are preferably such radicals in which W is a group of formula -CONH-, R_1 is hydrogen, methyl or ethyl, R_2 and R_3 are each hydrogen, Q is the radical -O- or -NH-, alk and alk_1 are each independently of the other ethylene or propylene, arylene is phenylene unsubstituted or substituted by methyl, methoxy, carboxy or by sulfo, Y is vinyl or β -sulfatoethyl, Y_1 is -CHBr-CH₂Br or -CBr=CH₂ and k is the number 0.

A fibre-reactive radical present in D₁ preferably corresponds to a radical of the above formula (3a), (3b), (3c), (3d), (3e) or (3f), wherein Y is vinyl, β -chloroethyl or β -sulfatoethyl, Hal is bromine, R_{1a} is hydrogen, m and n are each independently of the other the number 2 or 3, X_1 is halogen, T_1 is C₁-C₄alkoxy; C₁-C₄alkylthio; hydroxy; amino; N-mono- or N,N-di-C₁-C₄alkyl-amino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino or N-C₁-C₄alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy, and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthyl-amino unsubstituted or substituted by from 1 to 3 sulfo groups, or T_1 is a fibre-reactive radical of formula



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especially (4c') or (4d'), wherein

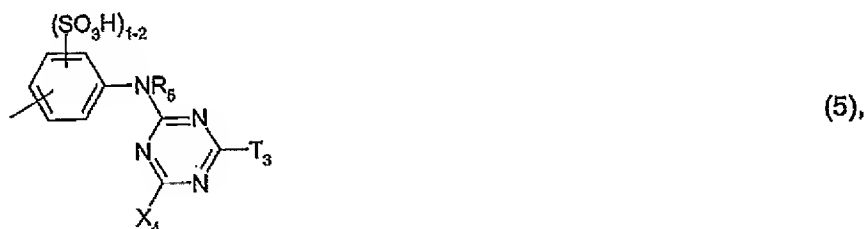
(R₄)₀₋₂ denotes from 0 to 2 identical or different substituents from the group halogen, C₁-C₄-alkyl, C₁-C₄alkoxy and sulfo, preferably from the group C₁-C₄alkyl, C₁-C₄alkoxy and sulfo and especially from the group methyl, methoxy and sulfo,

Y has the definition and preferred meanings given hereinabove, and

Y₁ is a -CH(Br)-CH₂-Br or -C(Br)=CH₂ group.

In the case of the radicals of formulae (4a') and (4b'), Y is preferably β-chloroethyl. In the case of the radicals of formulae (4c') and (4d'), Y is preferably vinyl or β-sulfatoethyl.

A preferred embodiment of the present invention relates to dyes wherein D₁ corresponds to a radical of formula



wherein

R₆ has the definition and preferred meanings given hereinabove for R₁, R_{1a} and R_{1b},

X₄ has the definition and preferred meanings given hereinabove for X₁, and is especially chlorine, and

T₃ is a monoazo- or disazo-amino radical of formula



wherein

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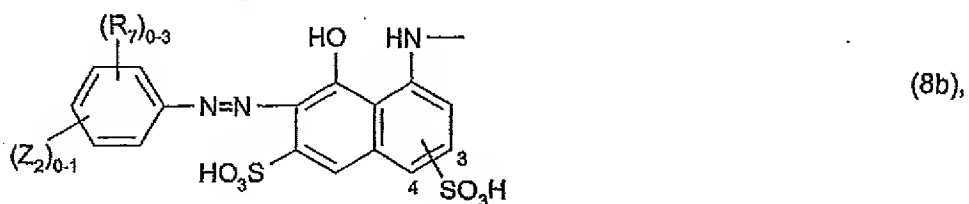
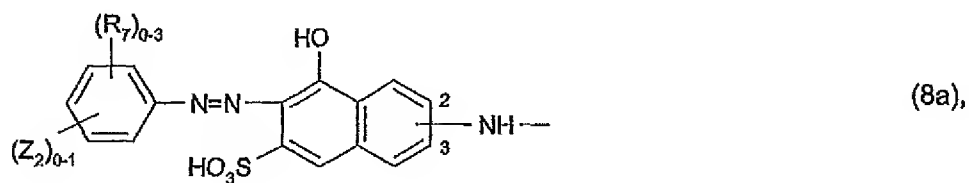
D_3 is the radical of a diazo component, of the benzene or naphthalene series, M is the radical of a middle component, of the benzene or naphthalene series, K_1 is the radical of a coupling component, of the benzene, naphthalene, pyrazolone, 6-hydroxypyridone-(2) or acetoacetic acid arylamide series, R_8 has the definition and preferred meanings given hereinabove for R_1 , R_{1a} and R_{1b} , and u is the number 0 or 1, wherein D_3 , M and K_1 may carry substituents customary for azo dyes.

The expression "substituents customary for azo dyes" is understood to include both fibre-reactive and non-fibre-reactive substituents, such as, for example, the substituents indicated above for D_1 .

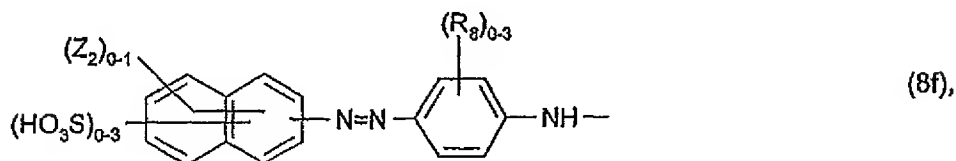
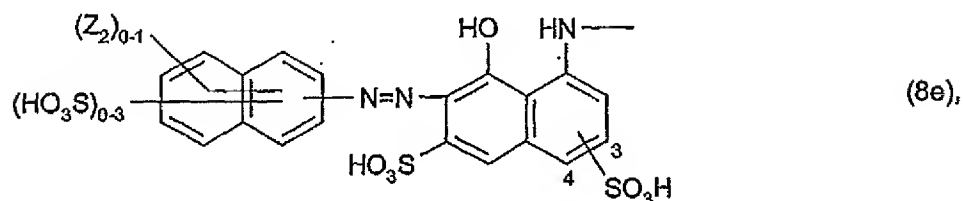
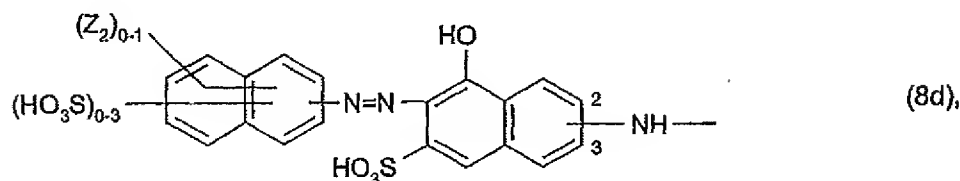
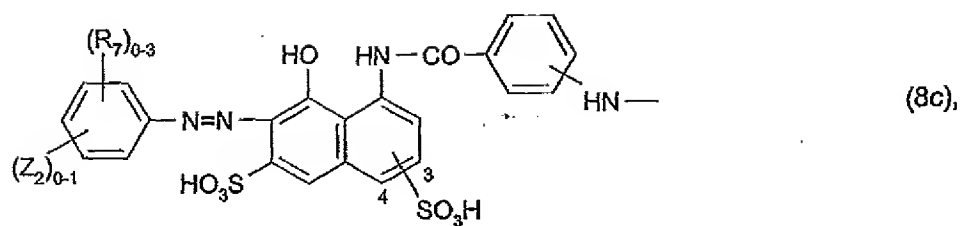
As non-fibre-reactive substituents for D_3 , M and K_1 in T_3 there come into consideration preferably C_1 - C_4 alkyl or C_1 - C_4 alkoxy each of which may themselves be substituted by hydroxy, C_1 - C_4 alkoxy, sulfo or by sulfato; halogen; carboxy; sulfo; nitro; cyano; trifluoromethyl; sulfamoyl; carbamoyl; amino; ureido; hydroxy; sulfomethyl; C_2 - C_4 alkanoylamino; C_1 - C_4 alkylsulfonylamino; benzoylamino unsubstituted or substituted on the phenyl ring by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen or by sulfo; and phenyl unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy or by sulfo.

The monoazo- or disazo-amino radicals of formula (6) or (7) contain preferably at least one sulfo group.

Preferred monoazo- and disazo-amino radicals T_3 are the radicals of formulae

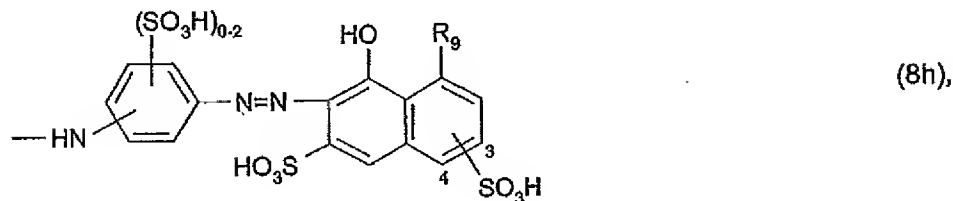
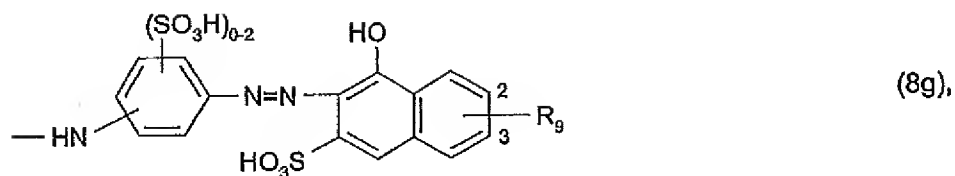


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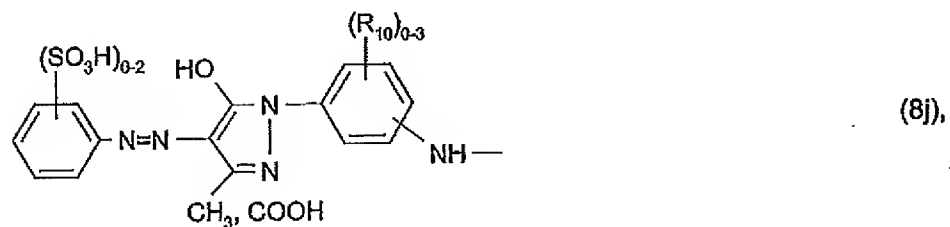
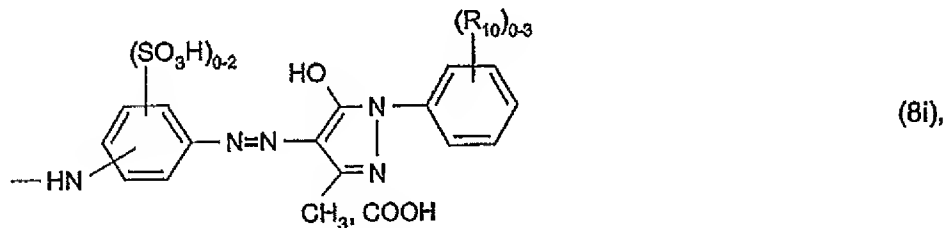


wherein $(\text{R}_7)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group $\text{C}_1\text{-C}_4$ -alkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_2\text{-C}_4$ alkanoylamino, halogen, carboxy and sulfo, $(\text{R}_8)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, $\text{C}_1\text{-C}_4$ alkyl; $\text{C}_1\text{-C}_4$ alkoxy unsubstituted or substituted by hydroxy, sulfato or by $\text{C}_1\text{-C}_4$ alkoxy; amino, $\text{C}_2\text{-C}_4$ alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, $\text{C}_1\text{-C}_4$ alkylsulfonfylamino and sulfo, preferably from the group halogen, $\text{C}_1\text{-C}_4$ alkyl; $\text{C}_1\text{-C}_4$ alkoxy unsubstituted or substituted by hydroxy, sulfato or by $\text{C}_1\text{-C}_4$ alkoxy; amino, $\text{C}_2\text{-C}_4$ alkanoylamino, ureido and sulfo, and Z_2 is a radical of formula (3a), (3b), (3c), (3d), (3e) or (3f), preferably (3a), (3b), (3c), (3d) or (3e) and especially (3a), the mentioned fibre-reactive radicals having the definitions and preferred meanings given hereinabove,

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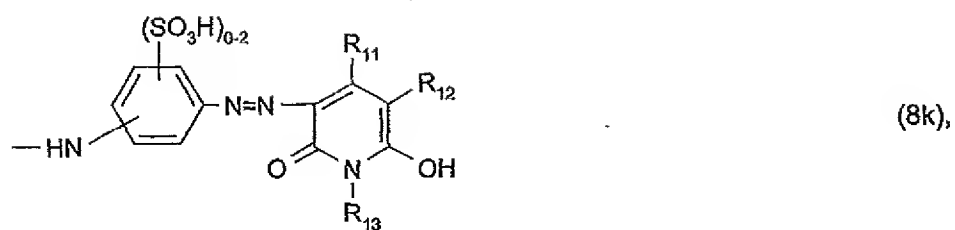


wherein R_9 is benzoylamino, C_2 - C_4 alkanoylamino, for example acetylamino or propionylamino, or a radical of the above formula (3f), preferably C_2 - C_4 alkanoylamino or benzoylamino, R_{1a} , T_1 and X_1 in the radical of formula (3f) each having the definitions and preferred meanings given hereinabove,

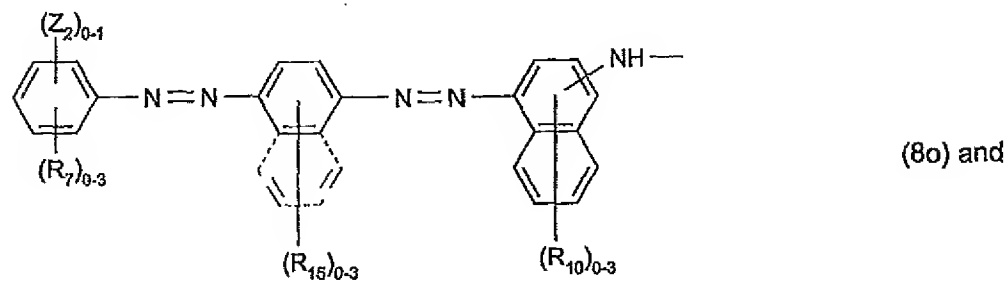
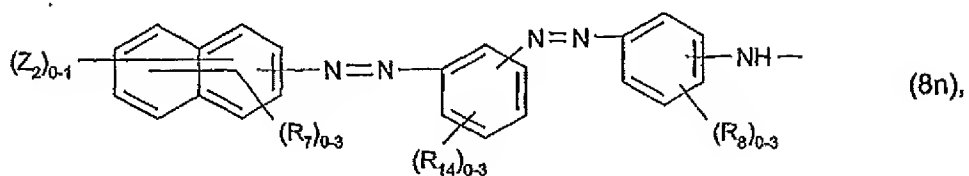
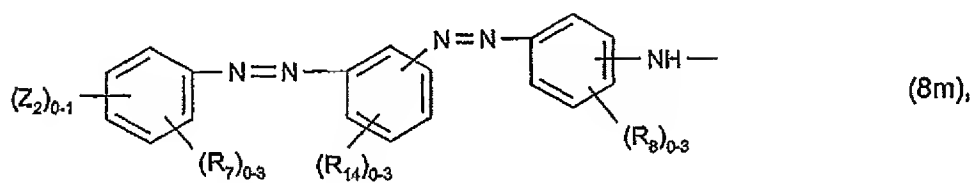
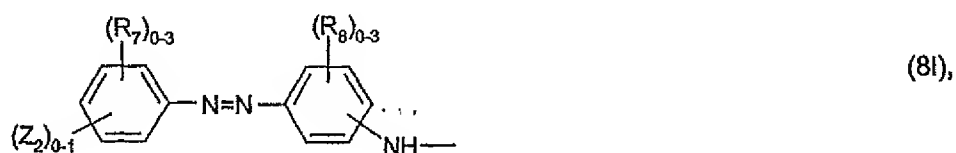


wherein $(R_{10})_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy and sulfo,

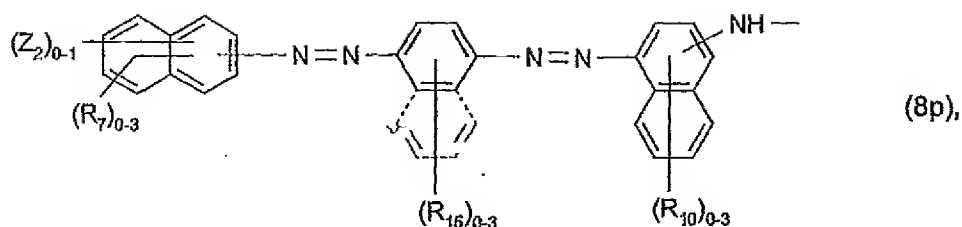
- 14 -



wherein R_{11} and R_{13} are each independently of the other hydrogen, C_1 - C_4 alkyl or phenyl, and R_{12} is hydrogen, cyano, carbamoyl or sulfomethyl,



- 15 -



wherein

$(R_7)_{0-3}$, $(R_8)_{0-3}$ and $(R_{10})_{0-3}$ each have the definitions and preferred meanings given hereinabove,

$(R_{14})_{0-3}$ and $(R_{15})_{0-3}$, each independently of the other, denotes from 0 to 3 identical or different substituents from the group C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxy and sulfo, and Z₂ has the definition and preferred meanings given hereinabove.

The numbers at the naphthyl rings of the radicals of formulae (8a), (8b), (8c), (8d), (8e), (8g) and (8h) indicate the preferred bonding positions.

The radicals $(R_7)_{0-3}$ in the disazoamino radicals of formulae (8n) and (8p) preferably denote from 0 to 3 sulfo groups.

In an embodiment of interest, Z₂ in the radicals of formulae (8a), (8b), (8c), (8d), (8e), (8f), (8i), (8m), (8n), (8o) and (8p) is hydrogen.

Especially preferred monoazo- and disazo-amino radicals T₃ are the radicals of formulae (8a), (8b), (8d), (8e), (8f), (8k) and (8m), especially (8b), (8e), (8k) and (8m).

In a further preferred embodiment of the present invention, D₁ is a radical of formula



preferably of formula (10), wherein D₄ is the radical of a diazo component, of the benzene or naphthalene series, K₂ is the radical of a coupling component, of the benzene, naphthalene, pyrazolone, 6-hydroxypyridone-(2) or acetoacetic acid arylamide series and K₃ is the radical of a coupling component, of the benzene or naphthalene series, wherein D₄, K₂ and K₃ may carry substituents customary for azo dyes.

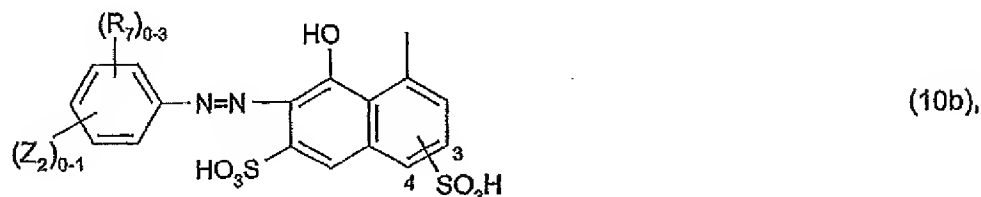
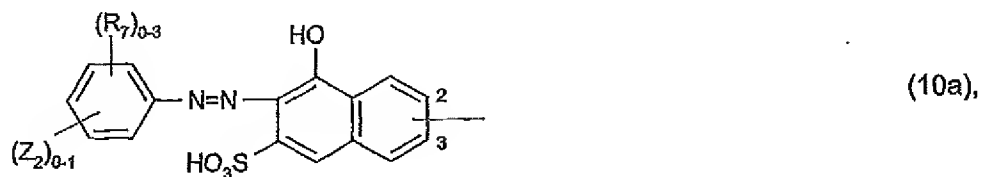
The expression "substituents customary for azo dyes" is understood to include both fibre-reactive and non-fibre-reactive substituents, such as, for example, the substituents indicated above for D₁.

As non-fibre-reactive substituents for D₄, K₂ and K₃ there come into consideration preferably C₁-C₄alkyl or C₁-C₄alkoxy each of which may themselves be substituted by hydroxy, C₁-C₄alkoxy, sulfo or by sulfato; halogen; carboxy; sulfo; nitro; cyano; trifluoromethyl; sulfamoyl; carbamoyl; amino; ureido; hydroxy; sulfomethyl; C₂-C₄alkanoylamino; C₁-C₄alkylsulfonylamino; benzoylamino unsubstituted or substituted on the phenyl ring by C₁-C₄alkyl, C₁-C₄alkoxy, halogen or by sulfo; and phenyl unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxy or by sulfo.

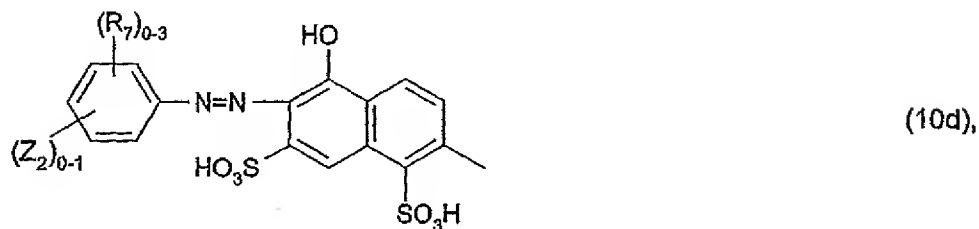
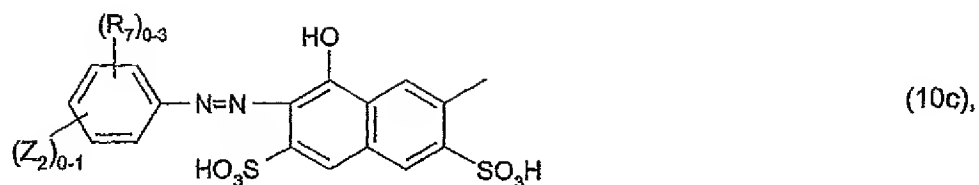
As fibre-reactive substituents for D₄, K₂ and K₃ there come into consideration preferably the radicals of formulae (3a), (3b), (3c), (3d), (3e) and (3f), especially (3a) and (3f) and more especially (3a), the said radicals having the definitions and preferred meanings given hereinabove. In an embodiment of interest, a radical of formula (3a) is preferred as fibre-reactive substituent for D₄ and a radical of formula (3f) is preferred as fibre-reactive substituent for K₃.

Monoazo radicals of formula (9) or (10) contain preferably at least one sulfo group.

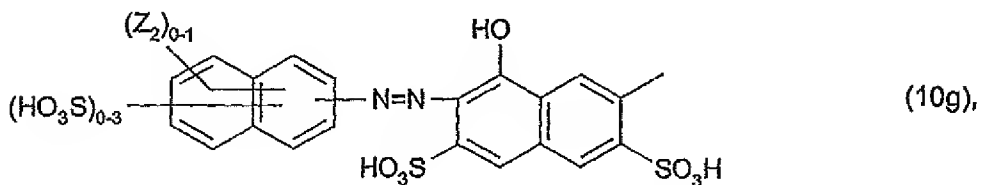
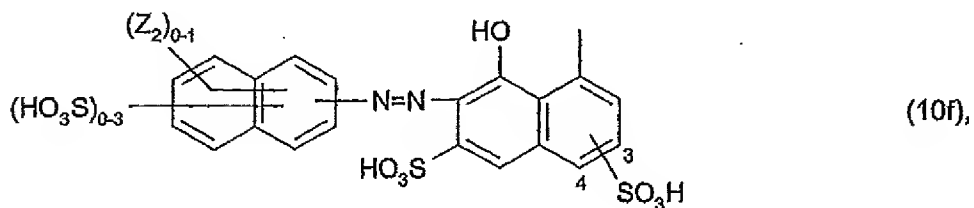
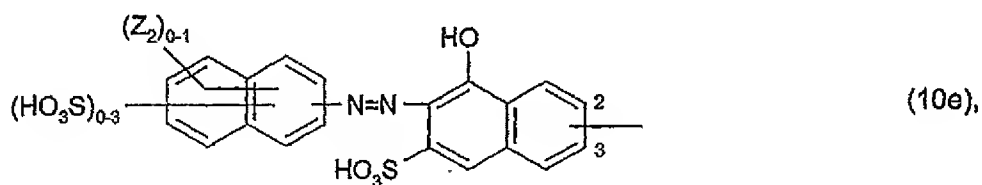
Preferred monoazo radicals D₁ of formula (10) correspond to the radicals of formulae



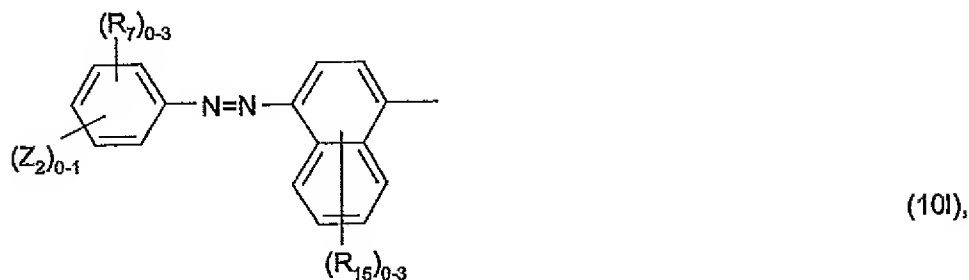
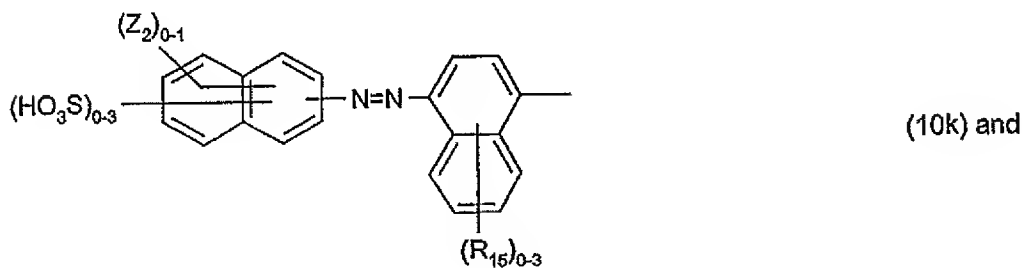
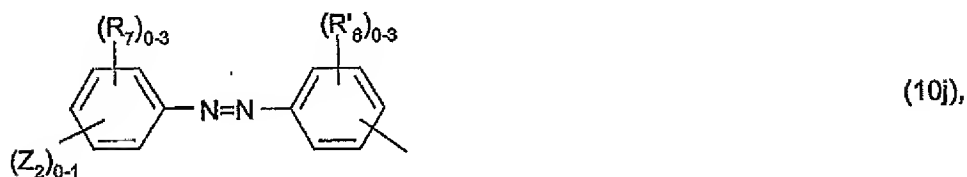
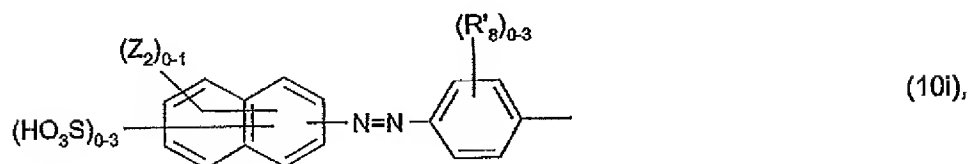
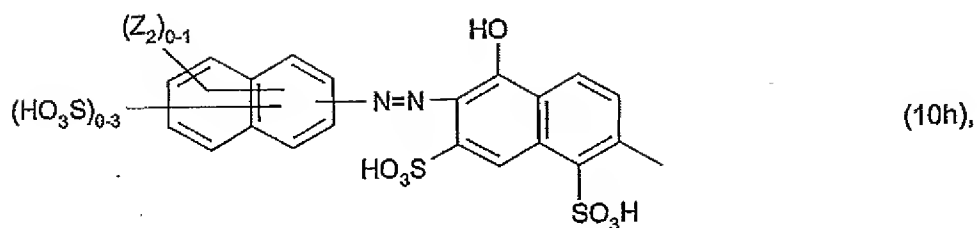
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wherein $(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1-C_4 alkyl, C_1-C_4 alkoxy, halogen, carboxy and sulfo and Z_2 is a fibre-reactive radical of formula (3a), (3c), (3d), (3e), (3f) or (3g), preferably (3a), (3c), (3d) or (3e) and especially (3a), wherein the said fibre-reactive radicals have the definitions and preferred meanings given hereinabove,



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wherein $(R_7)_{0-3}$ is as defined hereinabove, $(R'_8)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl; C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy; amino, C_2 - C_4 alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C_1 - C_4 alkylsulfonylamino,

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sulfo and a fibre-reactive radical of formula (3f), preferably from the group C₁-C₄alkyl; C₁-C₄alkoxy unsubstituted or substituted by hydroxy, sulfato or by C₁-C₄alkoxy; amino, C₂-C₄alkanoylamino, ureido, sulfo and a fibre-reactive radical of formula (3f), wherein R_{1a}, T₁ and X₁ in the radical of formula (3f) have the definitions and preferred meanings given hereinabove, (R₁₅)₀₋₃ denotes from 0 to 3 identical or different substituents from the group C₁-C₄alkyl, C₁-C₄alkoxy, halogen, carboxy and sulfo and is preferably sulfo, and Z₂ has the definition and preferred meanings given hereinabove.

The numbers at the naphthyl rings of the radicals of formulae (10a), (10b), (10e) and (10f) indicate the preferred bonding positions.

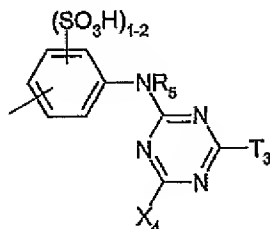
When R'₈ is a radical of formula (3f), then especially

R_{1a} is hydrogen,

T₁ is amino; N-mono- or N,N-di-C₁-C₄alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N-C₁-C₄alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring in the same way as phenylamino and in which alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and X₁ is chlorine.

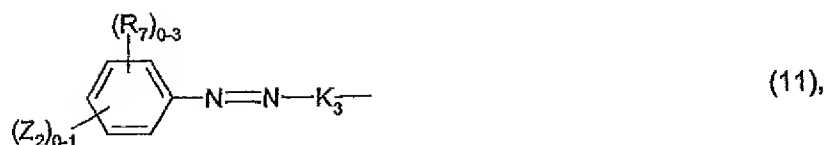
As a radical of formula (10), D₁ is especially preferably a radical of formula (10i), (10j), (10k) or (10l), especially of formula (10j) or (10l).

Preferably, the radical D₁ corresponds to a radical of formula (5) or (11)



(5) or

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wherein

R_5 is hydrogen or C_1 - C_4 alkyl, preferably hydrogen, methyl or ethyl and especially hydrogen, $(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy and sulfo, preferably from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino and sulfo,

X_4 is fluorine or chlorine, preferably chlorine,

T_3 is a radical of the above formula (8a), (8b), (8d), (8e), (8f), (8k) or (8m), preferably (8b), (8e), (8k) or (8m), wherein the variables have the definitions and preferred meanings given hereinabove,

Z_2 is a fibre-reactive radical of the above formula (3a), (3c), (3d), (3e), (3f) or (3g), preferably (3a), (3c), (3d) or (3e) and especially (3a), wherein the variables have the definitions and preferred meanings given hereinabove, and

K_3 is the radical of a coupling component of formula



wherein

R'_8 is hydrogen, sulfo, or C_1 - C_4 alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido or a radical of the above formula (3f), preferably hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino or

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ureido, wherein R_{1a} , T_1 and X_1 in the radical of formula (3f) have the definitions and preferred meanings given hereinabove, and, especially,

R_{1a} is hydrogen,

T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring in the same way as phenylamino and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and X_1 is chlorine.

There come into consideration as C_1 - C_4 alkyl for R_7 and R'_{8a} , each independently of the other, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and isobutyl, preferably methyl and ethyl and especially methyl.

There come into consideration as C_1 - C_4 alkoxy for R_7 , R'_8 and R'_{8a} , each independently of the others, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and isobutoxy, preferably methoxy and ethoxy. R_7 and R'_{8a} are especially methoxy. R'_8 is unsubstituted or may be substituted in the alkyl moiety by hydroxy or by sulfato.

There come into consideration as halogen for R_7 , each independently of any other(s), for example, fluorine, chlorine and bromine, preferably chlorine and bromine and especially chlorine.

There come into consideration as C_2 - C_4 alkanoylamino for R_7 and R'_{8a} , for example, acetylamino and propionylamino, especially acetylamino.

There comes into consideration as a radical of formula (3f) for R'_{8a} preferably a radical wherein

R_{1a} is hydrogen,

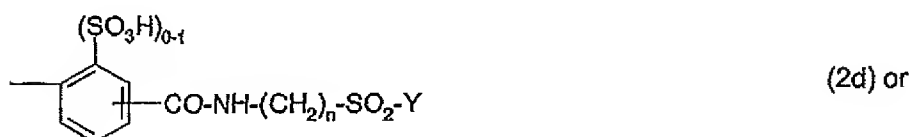
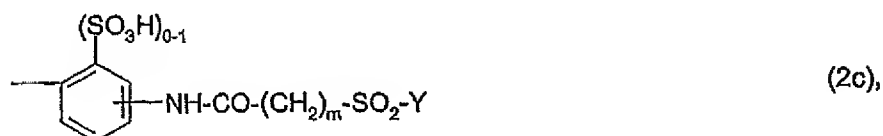
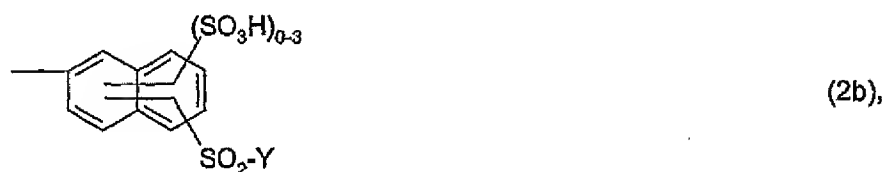
T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy and in which the alkyl is unsubstituted or substituted by

hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X_1 is fluorine or chlorine, preferably chlorine.

In an embodiment of interest, D_2 corresponds to a radical of formula (2), wherein $(Q_3)_{0-3}$ and Z_1 each have the definitions and preferred meanings given hereinabove.

Preferably, the radical D_2 corresponds to a radical of formula



wherein

$(R_3)_{0-2}$ denotes from 0 to 2 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy and sulfo, preferably from the group methyl, methoxy and sulfo, Y_1 is a $-CH(Br)-CH_2-Br$ or $-C(Br)=CH_2$ group,

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Y is vinyl or β -sulfatoethyl,

m is the number 2 or 3, preferably 2, and

n is the number 2 or 3, preferably 3.

Especially preferably, D_2 is a radical of the above formula (2a), (2b) or (2d), especially (2a);
in an embodiment of interest the radical of formula (2a) is a radical of formula



wherein

Y is vinyl or β -sulfatoethyl, and

the numbers given in the formula indicate the possible bonding positions of $-SO_2-Y$, the 4-position being preferred.

A preferred embodiment of the present invention relates to reactive dyes of formula (1)
wherein

Q_1 and Q_2 are hydrogen,

D_1 corresponds to a radical of the above formula (5) or (11) wherein

R_5 is hydrogen or C_1 - C_4 alkyl, preferably hydrogen, methyl or ethyl and especially hydrogen,
 $(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen,
 C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy and sulfo, preferably from the group
 C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino and sulfo,

X_4 is fluorine or chlorine, preferably chlorine,

T_3 is a radical of the above formula (8a), (8b), (8d), (8e), (8f), (8k) or (8m), preferably (8b),
(8e), (8k) or (8m), wherein the variables have the definitions and preferred meanings given
hereinabove,

Z_2 is a fibre-reactive radical of the above formula (3a), (3c), (3d), (3e), (3f) or (3g), preferably
(3a), (3c), (3d) or (3e) and especially (3a), wherein the variables have the definitions and
preferred meanings given hereinabove, and

K_3 is the radical of a coupling component of the above formula (12a) or (12b) wherein

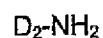
R'_8 is hydrogen, sulfo, or C_1 - C_4 alkoxy unsubstituted or substituted in the alkyl moiety by
hydroxy or by sulfato, and

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R'_{2a} is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido or a radical of the above formula (3f), wherein R_{1a} , T_1 and X_1 in the radical of formula (3f) have the definitions and preferred meanings given hereinabove, and D_2 is a radical of the above formula (2aa) wherein Y is vinyl or β -sulphatoethyl, and the numbers given in formula (2aa) indicate the possible bonding positions of $-SO_2-Y$, the 4-position being preferred.

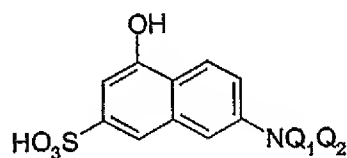
The present invention relates also to a process for the preparation of dyes of formula (1) which comprises

(i) diazotisation of approximately one molar equivalent of an amine of formula



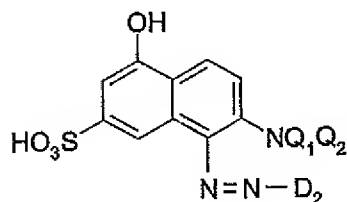
(13)

In customary manner and reaction with approximately one molar equivalent of a compound of formula



(14)

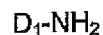
to form a compound of formula



(15a);

and

(ii) diazotisation of approximately one molar equivalent of an amine of formula



(16)

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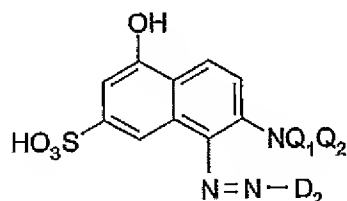
in customary manner and reaction with approximately one molar equivalent of the compound of formula (15a) obtained according to (i) to form a compound of formula (1) wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions and preferred meanings given hereinabove.

The diazotisation of the amines of formulae (13) and (16) is carried out in a manner known *per se*, for example using a nitrite, for example an alkali metal nitrite such as sodium nitrite, in a mineral acid medium, for example in a hydrochloric acid medium, at temperatures of, for example, from -5 to 40°C and preferably at from 0 to 20°C.

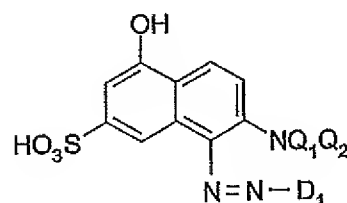
The coupling to the coupling components of formulae (14) and (15a) is carried out in a manner known *per se* at acidic or neutral to slightly alkaline pH values, for example a pH value of from 0 to 8, and at temperatures of, for example, from -5 to 40°C, preferably from 0 to 30°C.

The first coupling - (i) - takes place in an acidic medium, for example at a pH of from 0 to 4, and the second coupling - (ii) - at elevated pH values, in a slightly acidic, neutral or slightly alkaline medium, for example a pH value of from 4 to 8.

By proceeding as described hereinabove but, instead of using approximately one molar equivalent each of the amines of formulae (13) and (16) in process steps (i) and (ii), using in each case approximately one molar equivalent of a mixture of at least two, preferably two, non-identical amines, for example a 1:1 molar mixture of the compounds of formulae (13) and (16), there is obtained first of all, according to (i), a mixture of compounds of formulae



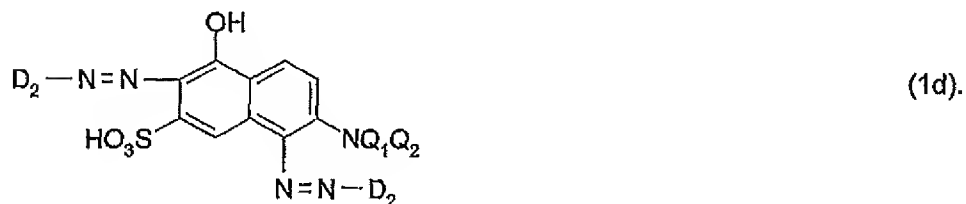
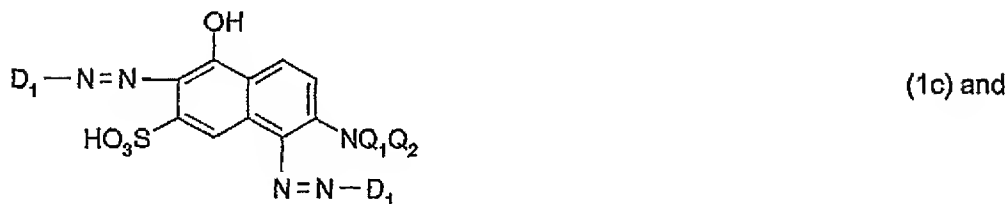
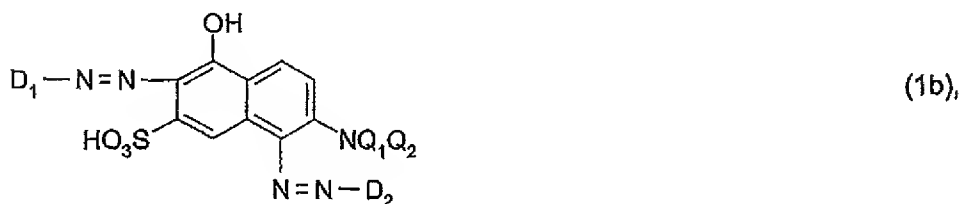
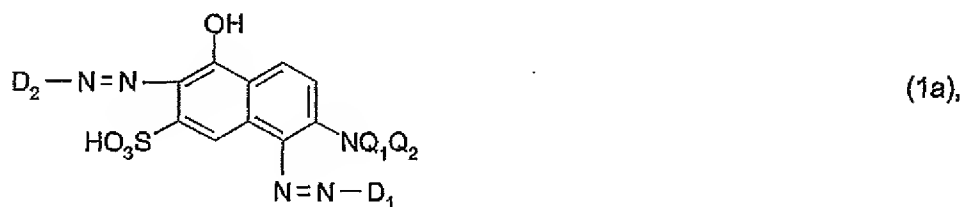
(15a) and



(15b)

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and, on further reaction of the mixture of compounds of formulae (15a) and (15b) according to (ii), a mixture of dyes of formulae (1a), (1b), (1c) and (1d)



The present invention accordingly relates also to dye mixtures that comprise at least one dye of formulae (1a) and (1b) together with at least one dye of formulae (1c) and (1d), especially one dye each of formulae (1a), (1b), (1c) and (1d), wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions and preferred meanings given hereinabove and D_1 and D_2 are not identical.

The ratio of the dyes of formulae (1a), (1b), (1c) and (1d) in the mixture can vary within wide limits and depends on the ratio of the particular amines D_1-NH_2 and D_2-NH_2 used according to (i) and (ii).

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The above dye mixtures contain, for example, from 5 to 95 % by weight, especially from 10 to 90 % by weight and preferably from 20 to 80 % by weight, of a dye of formula (1a) and/or (1b), based on the total amount of the dyes of formulae (1a), (1b), (1c) and (1d) in the mixture.

Where appropriate, the end product may, in addition, be subjected to a conversion reaction. Such a conversion reaction is, for example, the conversion of the radical Y denoting $-\text{CH}_2\text{CH}_2-\text{U}$ or another reactive group capable of conversion to a vinyl moiety into the corresponding vinyl form by treatment with dilute sodium hydroxide solution, such as, for example, the conversion of the β -sulfatoethylsulfonyl or β -chloroethylsulfonyl group into the vinylsulfonyl radical. Such reactions are known *per se*.

The compounds of formulae (13), (14) and (16) are known or can be obtained in a manner known *per se*.

For example, the compound of formula (16) wherein D_1 is a radical of the above formula (5) can be prepared by condensation of approximately one molar equivalent of 2,4,6-trichloro-s-triazine or 2,4,6-trifluoro-s-triazine first with approximately one molar equivalent of a compound of formula



at a pH value in the neutral range and at low temperature, for example from 0 to 5°C, and then with approximately one molar equivalent of a compound of formula



at a slightly acidic to neutral pH value, for example pH 4.5-7.5, and at a temperature of, for example, from 0 to 30°C.

Such condensation reactions are known and are described, for example, in EP-A-0 260 227 and US-A-4 841 049.

Instead of the compound of formula (17), a preliminary product, for example a diazo component or coupling component, may alternatively be used in the process, the radical T_3 being produced only in the further course of the process by a corresponding diazotisation and coupling reaction.

The reactive dyes according to the invention are either in the form of their free acids or, preferably, in the form of salts thereof. Salts that come into consideration are, for example, alkali metal, alkaline earth metal and ammonium salts, and salts of an organic amine. Sodium, lithium, potassium and ammonium salts and the salt of the mono-, di- or tri-ethanolamine may be mentioned as examples.

The reactive dyes according to the invention are suitable for dyeing and printing an extremely wide variety of materials, especially hydroxyl-group-containing or nitrogen-containing fibre materials. Examples are paper, silk, leather, wool, polyamide fibres and polyurethanes and also especially cellulosic fibre materials of all kinds. Such fibre materials are, for example, natural cellulosic fibres, such as cotton, linen and hemp, and also cellulose and regenerated cellulose. The dyes according to the invention are also suitable for dyeing or printing hydroxyl-group-containing fibres present in blend fabrics, e.g. blends of cotton with polyester fibres or polyamide fibres.

The present invention accordingly relates also to the use of the reactive dyes according to the invention in the dyeing or printing of hydroxyl-group-containing or nitrogen-containing, especially cotton-containing, fibre materials.

The reactive dyes according to the invention can be applied to the fibre material and fixed to the fibre in a variety of ways, especially in the form of aqueous dye solutions and dye print pastes. They are suitable both for the exhaust method and for dyeing in accordance with the pad-dyeing method; they can be used at low dyeing temperatures and require only short steaming times in the pad-steam process. The degrees of fixing are high and unfixed dye can be washed off easily, the difference between the degree of exhaust and the degree of fixing being remarkably small, that is to say the soaping loss being very low. The reactive

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dyes according to the invention are also suitable for printing, especially on cotton, but are equally suitable also for printing nitrogen-containing fibres, for example wool or silk or blend fabrics that contain wool.

The dyeings and prints produced using the reactive dyes according to the invention have a high tinctorial strength and a high fibre-to-dye binding stability in both the acidic and the alkaline range, and furthermore have good fastness to light and very good wet-fastness properties, such as fastness to washing, to water, to sea water, to cross-dyeing and to perspiration. The dyeings obtained exhibit fibre levelness and surface levelness.

The present invention relates furthermore to aqueous inks that comprise a reactive dye of formula (1) wherein Q_1 , Q_2 , D_1 and D_2 each have the definitions and preferred meanings given hereinabove.

The dyes used in the inks should preferably have a low salt content, that is to say they should have a total content of salts of less than 0.5 % by weight, based on the weight of the dyes. Dyes that have relatively high salt contents as a result of their preparation and/or as a result of the subsequent addition of diluents can be desalted, for example, by membrane separation procedures, such as ultrafiltration, reverse osmosis or dialysis.

The inks preferably have a total content of dyes of from 1 to 35 % by weight, especially from 1 to 30 % by weight and preferably from 1 to 20 % by weight, based on the total weight of the ink. The preferred lower limit in this case is a limit of 1.5 % by weight, preferably 2 % by weight and especially 3 % by weight.

The inks may comprise water-miscible organic solvents, for example C_1 - C_4 alcohols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol or isobutanol; amides, e.g. dimethylformamide or dimethylacetamide; ketones or ketone alcohols, e.g. acetone, diacetone alcohol; ethers, e.g. tetrahydrofuran or dioxane; nitrogen-containing heterocyclic compounds, e.g. N-methyl-2-pyrrolidone or 1,3-dimethyl-2-imidazolidone, polyalkylene glycols, e.g. polyethylene glycol or polypropylene glycol; C_2 - C_6 alkylene glycols and thioglycols, e.g. ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, thiodiglycol, hexylene glycol and diethylene glycol; other polyols, e.g. glycerol or 1,2,6-hexanetriol; and C_1 - C_4 alkyl ethers of polyhydric alcohols, e.g. 2-methoxyethanol, 2-(2-methoxy-

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ethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol or 2-[2-(2-ethoxyethoxy)ethoxy]ethanol; preferably N-methyl-2-pyrrolidone, diethylene glycol, glycerol or especially 1,2-propylene glycol, usually in an amount of from 2 to 30 % by weight, especially from 5 to 30 % by weight and preferably from 10 to 25 % by weight, based on the total weight of the ink.

In addition, the inks may also comprise solubilisers, e.g. ϵ -caprolactam.

The inks may comprise thickeners of natural or synthetic origin *inter alia* for the purpose of adjusting the viscosity.

Examples of thickeners that may be mentioned include commercially available alginate thickeners, starch ethers or locust bean flour ethers, especially sodium alginate on its own or in admixture with modified cellulose, e.g. methyl cellulose, ethyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, methyl hydroxyethyl cellulose, hydroxypropyl cellulose or hydroxypropyl methyl cellulose, especially with preferably from 20 to 25 % by weight carboxymethyl cellulose. Synthetic thickeners that may be mentioned are, for example, those based on poly(meth)acrylic acids or poly(meth)acrylamides.

The inks comprise such thickeners, for example, in an amount of from 0.01 to 2 % by weight, especially from 0.01 to 1 % by weight and preferably from 0.01 to 0.5 % by weight, based on the total weight of the ink.

The inks may also comprise buffer substances, e.g. borax, borates, phosphates, polyphosphates or citrates. Examples that may be mentioned include borax, sodium borate, sodium tetraborate, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium tripolyphosphate, sodium pentapolyphosphate and sodium citrate. They are used especially in amounts of from 0.1 to 3 % by weight, preferably from 0.1 to 1 % by weight, based on the total weight of the ink, in order to establish a pH value of, for example, from 4 to 9, especially from 5 to 8.5.

As further additives, the inks may comprise surfactants or humectants.

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Suitable surfactants include commercially available anionic or non-ionic surfactants. As humectants in the inks according to the invention there come into consideration, for example, urea or a mixture of sodium lactate (advantageously in the form of a 50 % to 60 % aqueous solution) and glycerol and/or propylene glycol in amounts of preferably from 0.1 to 30 % by weight, especially from 2 to 30 % by weight.

Preference is given to inks having a viscosity of from 1 to 40 mPa·s, especially from 1 to 20 mPa·s and more especially from 1 to 10 mPa·s.

Furthermore, the inks may in addition comprise customary additives, e.g. anti-foams or especially substances that inhibit fungal and/or bacterial growth. Such additives are usually used in amounts of from 0.01 to 1 % by weight, based on the total weight of the ink.

The inks can be prepared in customary manner by mixing together the individual constituents in the desired amount of water.

The inks according to the invention are suitable especially for use in recording systems of a kind in which an ink is forced out of a small aperture in the form of droplets that are directed onto a substrate on which an image is formed. Suitable substrates are, for example, paper, textile fibre materials or plastics films. Suitable recording systems are, for example commercially available ink-jet printers for use in paper or textile printing, or writing instruments, such as fountain pens or ballpoint pens, and especially inkjet printers.

Depending on the use, it may be necessary, for example, for the viscosity or other physical properties of the ink, especially properties that have an influence on the affinity for the substrate in question, to be adapted accordingly.

As examples of paper that can be printed with the inks according to the invention there may be mentioned commercially available ink-jet paper, photo paper, glossy paper, plastics-coated paper, e.g. Epson Ink-jet Paper, Epson Photo Paper, Epson Glossy Paper, Epson Glossy Film, HP Special Ink-jet Paper, Encad Photo Gloss Paper and Ilford Photo Paper. Plastics films that can be printed with the inks according to the invention are, for example, transparent or cloudy/opaque. Suitable plastics films are, for example, 3M Transparency Film.

As textile fibre materials there come into consideration, for example, nitrogen-containing or hydroxy-group-containing fibre materials, for example textile fibre materials of cellulose, silk, wool or synthetic polyamides, preferably cellulose.

The present invention accordingly relates also to a method of printing textile fibre materials, paper or plastics films, preferably textile fibre materials or paper, and especially textile fibre materials, according to the ink-jet printing method, which comprises using an aqueous ink that comprises a reactive dye of formula (1) wherein Q_1 , Q_2 , D_1 and D_2 each have the definitions and preferred meanings given hereinabove.

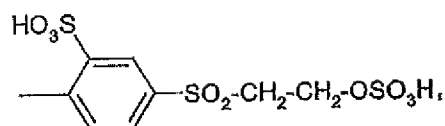
In the case of the ink-jet printing method, individual droplets of ink are sprayed onto a substrate from a nozzle in a controlled manner. It is mainly the continuous ink-jet method and the drop-on-demand method that are used for that purpose. In the case of the continuous ink-jet method, the droplets are produced continuously, droplets not required for the printing operation being discharged into a receptacle and recycled. In the case of the drop-on-demand method, on the other hand, droplets are generated as desired and used for printing; that is to say, droplets are generated only when required for the printing operation. The production of the droplets can be effected, for example, by means of a piezo ink-jet head or by thermal energy (bubble jet). For the process according to the invention, printing by means of a piezo ink-jet head is preferred, but preference is given also to printing according to the continuous ink-jet method.

The recordings, for example prints, produced are distinguished especially by a high tinctorial strength and a high colour brilliancy as well as by good light-fastness and wet-fastness properties.

The following Examples serve to illustrate the invention. Unless otherwise indicated, the temperatures are given in degrees Celsius, parts are parts by weight and percentages relate to % by weight. Parts by weight relate to parts by volume in a ratio of kilograms to litres.

Example 1: 32.5 parts of an amine of formula $D_{10}\text{-NH}_2$, wherein D_{10} is a radical of formula

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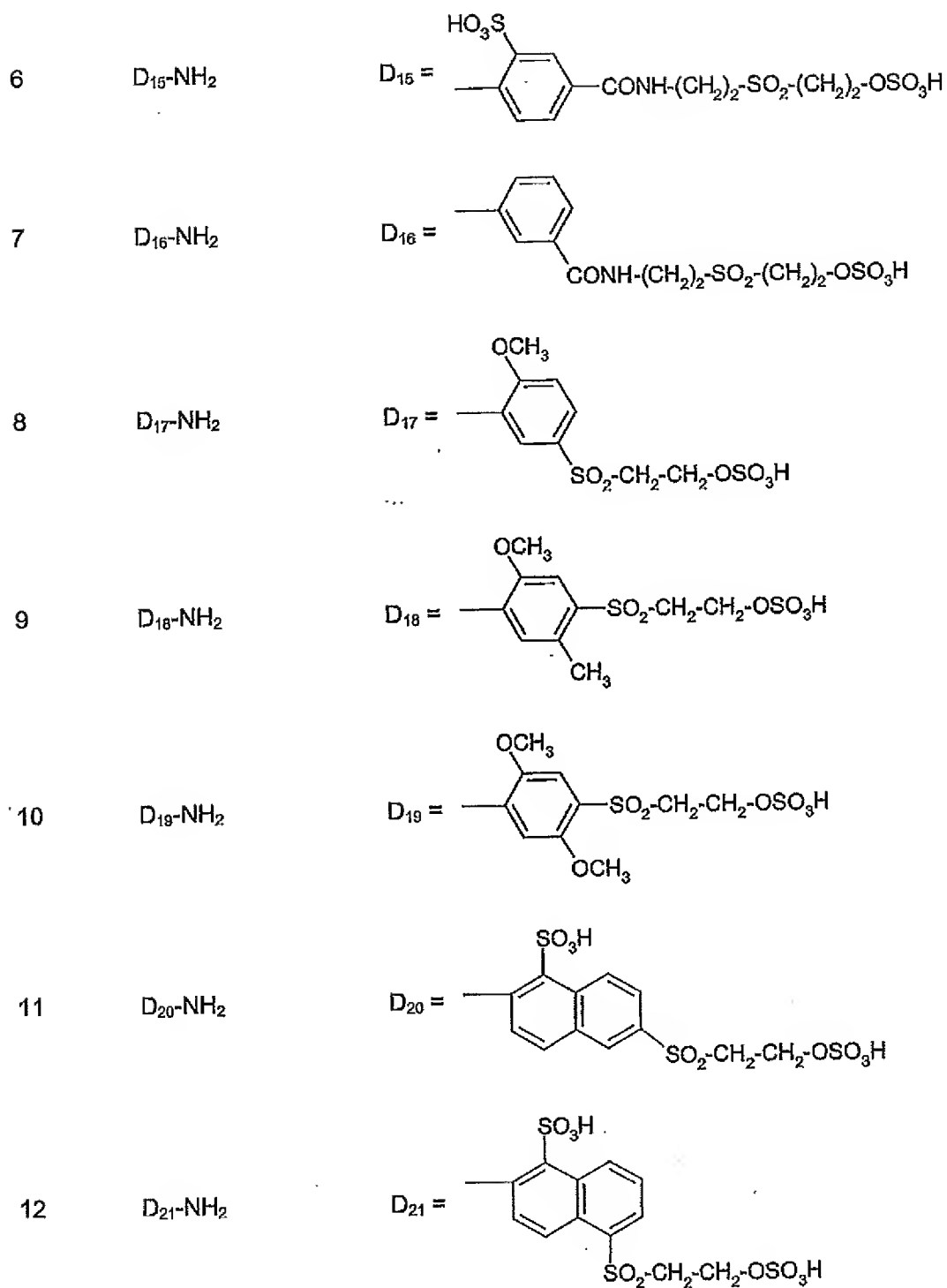
are introduced into 100 parts of water and stirred well. At 10°C, there are added to the resulting suspension first of all 22.8 parts of a 4N sodium nitrite solution and then 41 parts of a 31 % naphthalenesulfonic acid solution. Stirring is then carried out for 3 hours at from 15 to 20°C.

Examples 2 to 19: The diazo compounds of the amines indicated in Table 1 can be prepared analogously to the procedure described in Example 1 by using, instead of the amine of formula $D_{10}\text{-NH}_2$ mentioned in Example 1, an equimolar amount of the amines of formula $D_{xy}\text{-NH}_2$ indicated in Table 1.

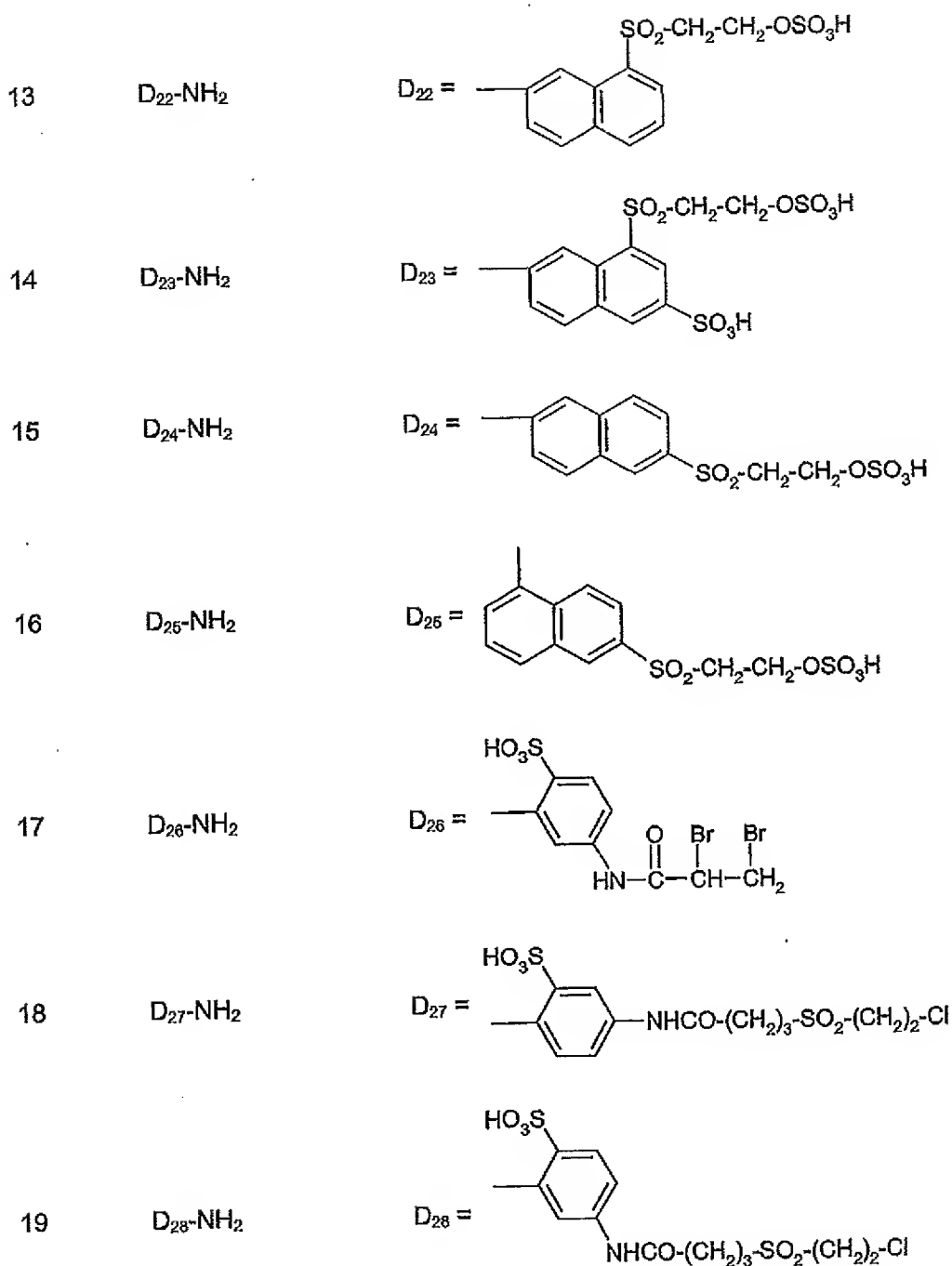
Table 1:

Ex.	Amine $D_{xy}\text{-NH}_2$	D_{xy}
2	$D_{11}\text{-NH}_2$	$D_{11} = $
3	$D_{12}\text{-NH}_2$	$D_{12} = $
4	$D_{13}\text{-NH}_2$	$D_{13} = $
5	$D_{14}\text{-NH}_2$	$D_{14} = $

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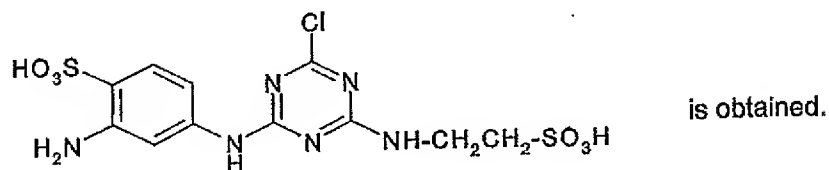
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**Example 20:**

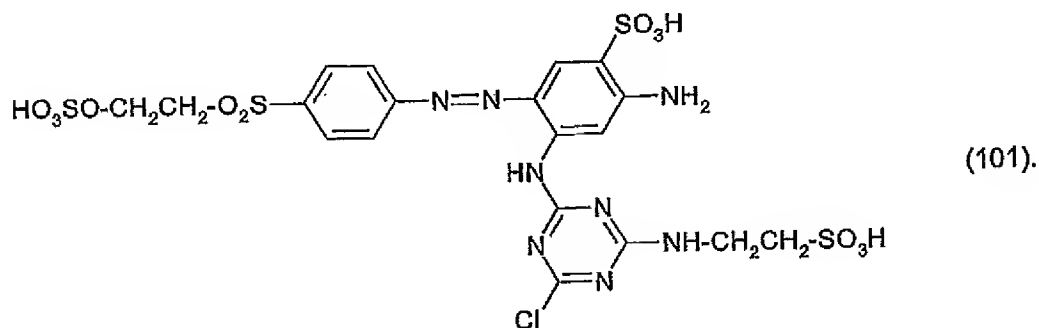
a) 36.9 parts of cyanuric chloride are stirred in 150 parts of ice/water and a small amount of wetting agent. At from 0 to 2°C, a solution of 25.25 parts of taurine in 50 parts of water is introduced in the course of 40 minutes and condensation is carried out at a pH of from 7 to 8

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by the dropwise addition of 2N sodium hydroxide solution. Stirring is then carried out at from 0 to 5°C and a pH of from 7 to 7.5 until cyanuric chloride can no longer be detected. A neutral solution of 39.48 parts of 1,3-phenylenediamine-4-sulfonic acid in 100 parts of water is then added. Condensation is carried out at a temperature of from 5 to 20°C and the pH is maintained at from 8 to 9 by the addition of 2N sodium hydroxide solution. When condensation is complete, the reaction solution is salted out using KCl, filtered and washed with concentrated KCl solution. After drying, the intermediate of formula



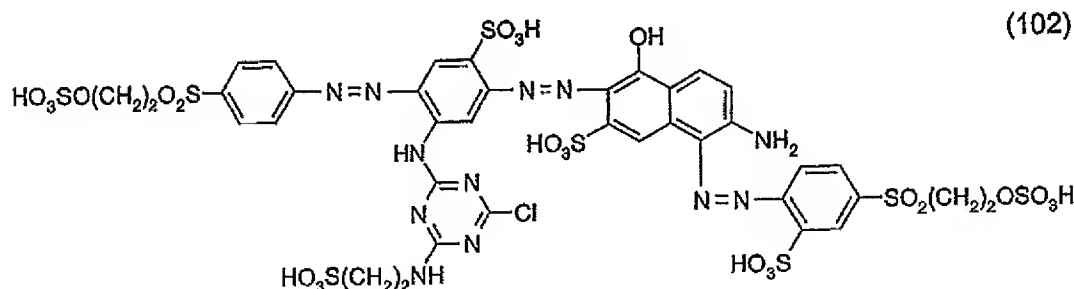
b) 68 parts of the compound according to a) are suspended in 300 parts of water. The diazotized amine from Example 3, which is prepared according to Example 1 from 45 parts of the amine of formula D₁₂-NH₂, is then added in the course of 10 minutes at from 0 to 5°C, and the pH is maintained at from 6 to 8.5 using soda solution (20 %). When coupling is complete, the yellow dye is precipitated using KCl, and the suspension obtained is filtered and dried *in vacuo*, yielding the monoazo compound of formula



c) 83 parts of the compound according to Example b) are dissolved in 700 parts of water and diazotized according to the customary method with sodium nitrite and HCl at from 0 to 5°C.

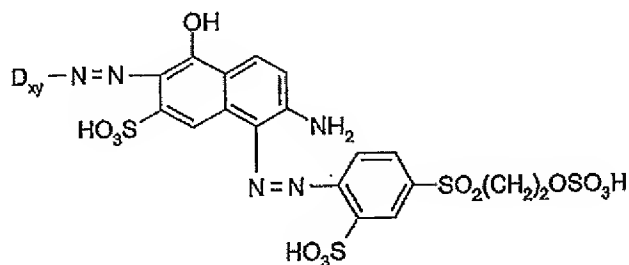
Example 21:

A solution of 21.5 parts of 2-amino-5-naphthol-7-sulfonic acid in 250 parts of water (pH 7) is added dropwise at from 0 to 5°C to the acid suspension of the diazo compound of the amine of formula D₁₀-NH₂ obtained according to Example 1. The mixture is then heated to room temperature and stirred for approximately 5 h until coupling is complete (first coupling). The reaction mixture is then cooled to from 5 to 10°C, the pH value is increased to approximately 4.5 using an aqueous sodium hydrogen carbonate solution, and the suspension of the diazo compound obtained according to Example 20c) is slowly added dropwise, the pH value being maintained during the dropwise addition at approximately 4.5 by the addition of an aqueous sodium hydrogen carbonate solution and the temperature being maintained at approximately 5°C. After the dropwise addition, the pH value is adjusted to 6 (second coupling). When coupling is complete, the dye solution is freed of salt by dialysis and concentrated by evaporation *in vacuo*. A compound is obtained which in the form of the free acid corresponds to formula



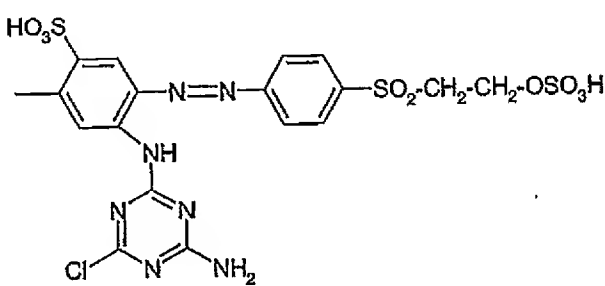
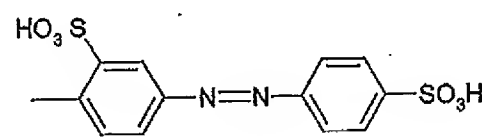
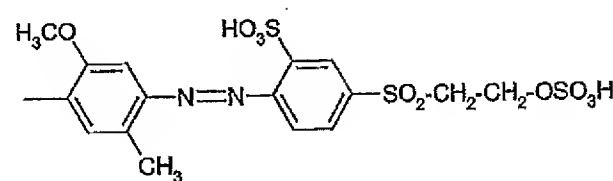
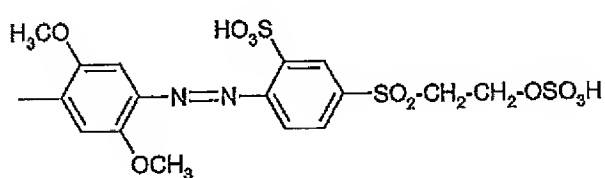
(λ_{\max} : 550 nm), which dyes wool and cellulose in a bluish violet shade having good allround fastness properties.

Examples 22 to 39v: A compound of the general formula

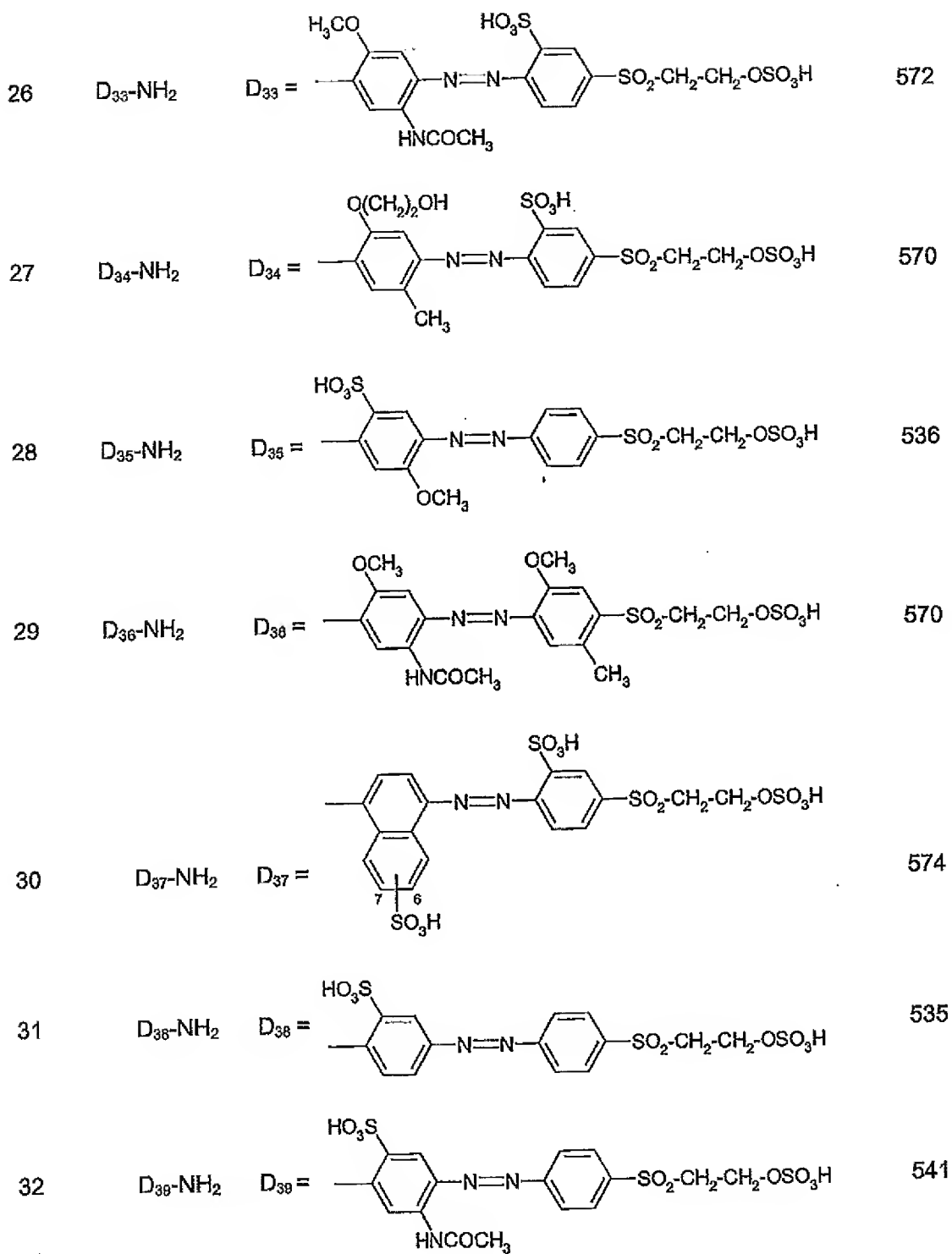


can be prepared analogously to the procedure described in Example 21 by using, instead of the amine of formula (101), an equimolar amount of one of the amines of formula $D_{xy}\text{-NH}_2$ indicated in Table 2. The dyes dye wool and cellulose in orange to blue shades having good allround fastness properties.

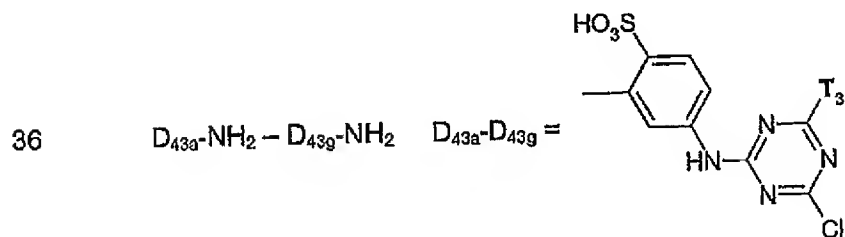
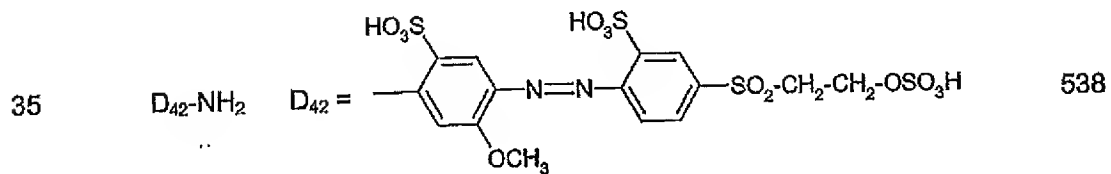
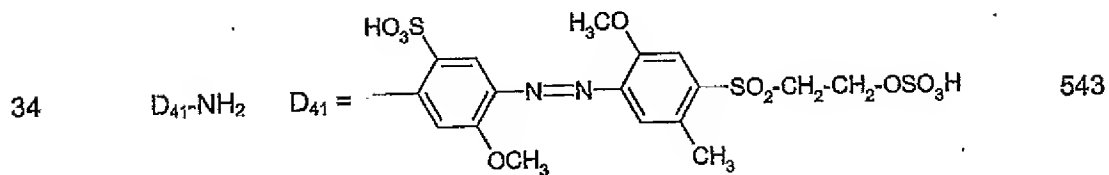
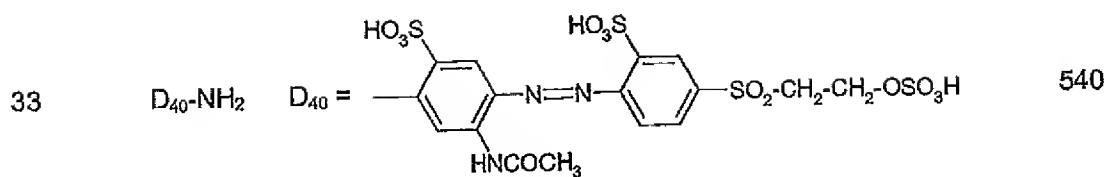
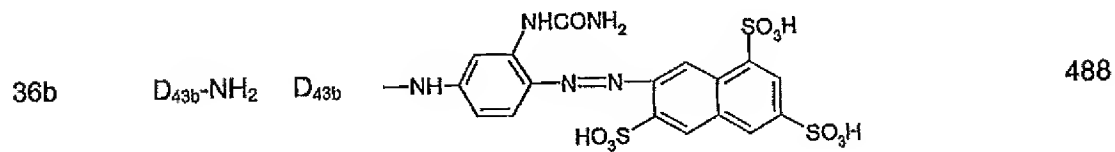
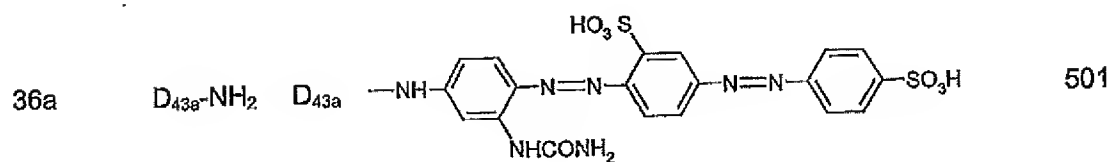
Table 2:

Ex.	Amine $D_{xy}\text{-NH}_2$	D_{xy}	λ_{max} [nm]
22	$D_{29}\text{-NH}_2$	$D_{29} = $ 	550
23	$D_{30}\text{-NH}_2$	$D_{30} = $ 	536
24	$D_{31}\text{-NH}_2$	$D_{31} = $ 	570
25	$D_{32}\text{-NH}_2$	$D_{32} = $ 	583

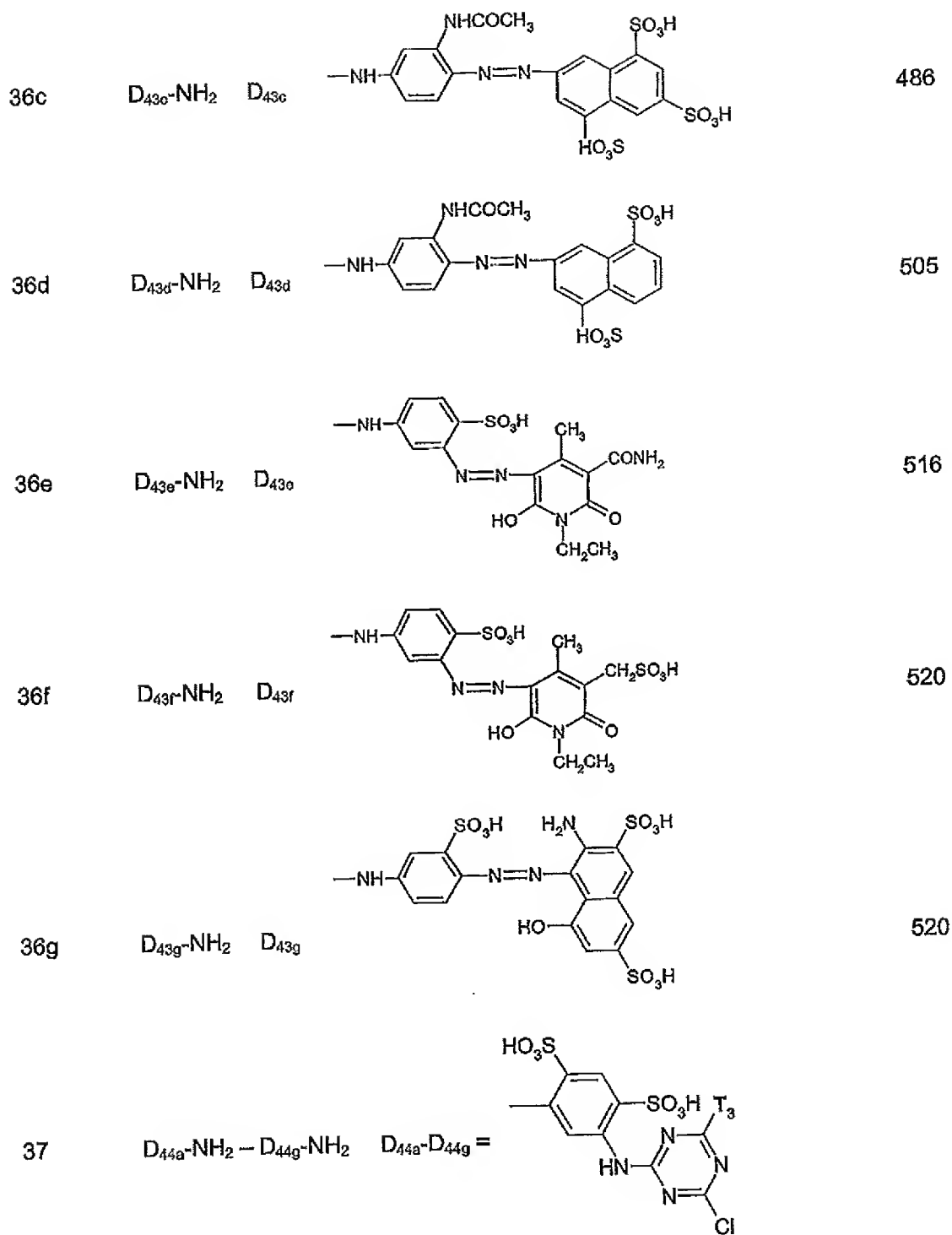
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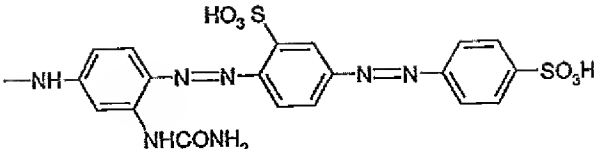
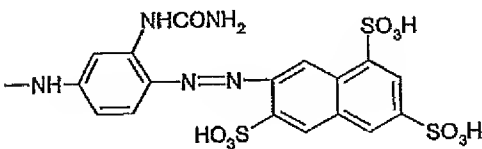
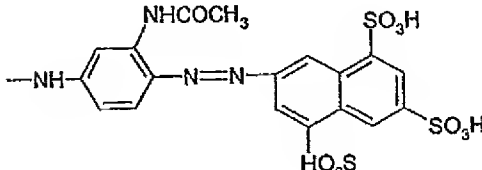
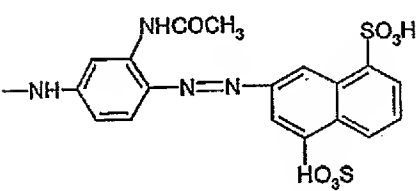
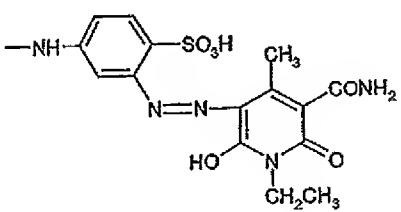
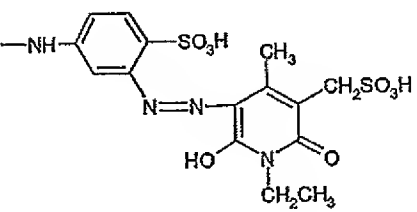
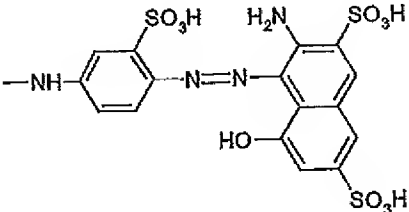
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 T_3 :

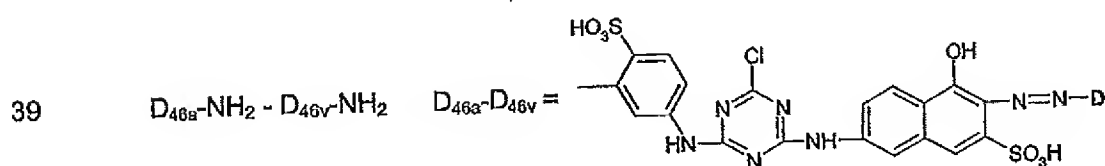
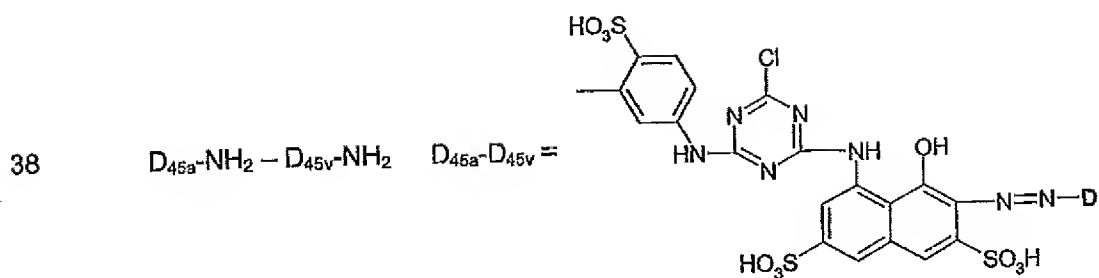
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T₃:

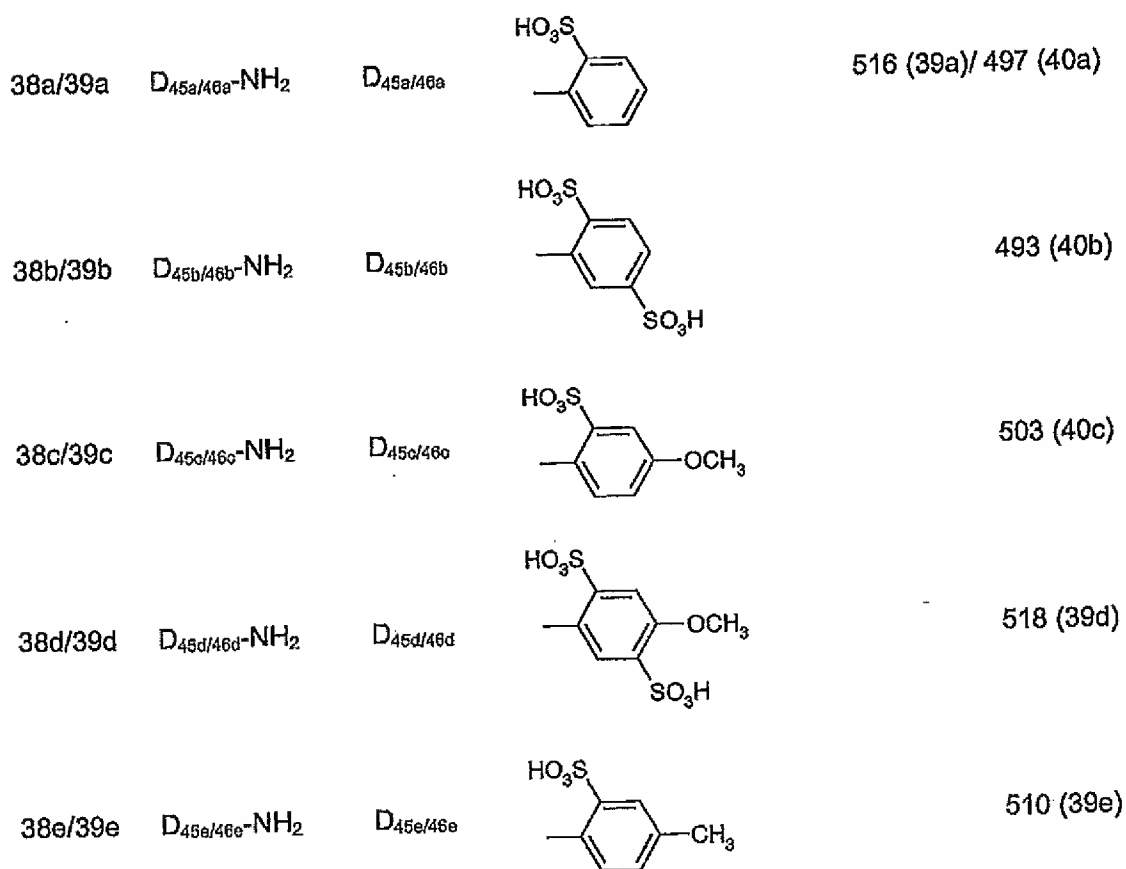
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37a	D _{44a} -NH ₂	D _{44a}		495
37b	D _{44b} -NH ₂	D _{44b}		489
37c	D _{44c} -NH ₂	D _{44c}		487
37d	D _{44d} -NH ₂	D _{44d}		497
37e	D _{44e} -NH ₂	D _{44e}		514
37f	D _{44f} -NH ₂	D _{44f}		513
37g	D _{44g} -NH ₂	D _{44g}		514

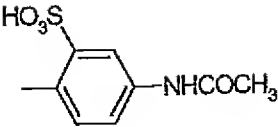
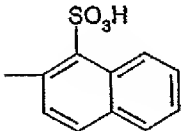
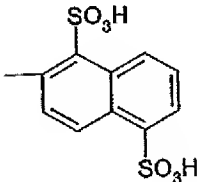
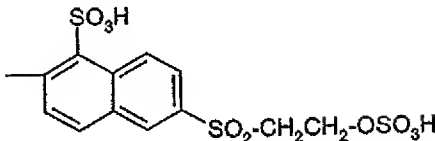
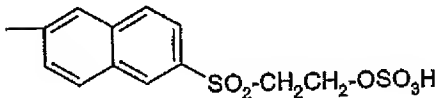
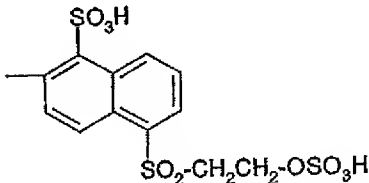
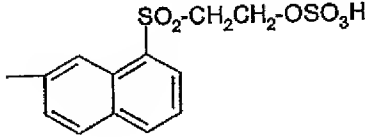
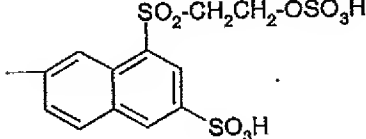
- 43 -



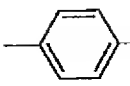
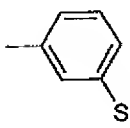
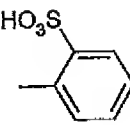
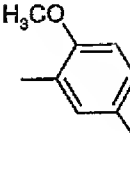
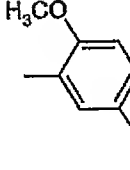
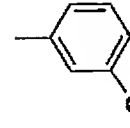
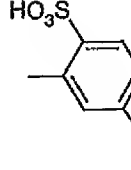
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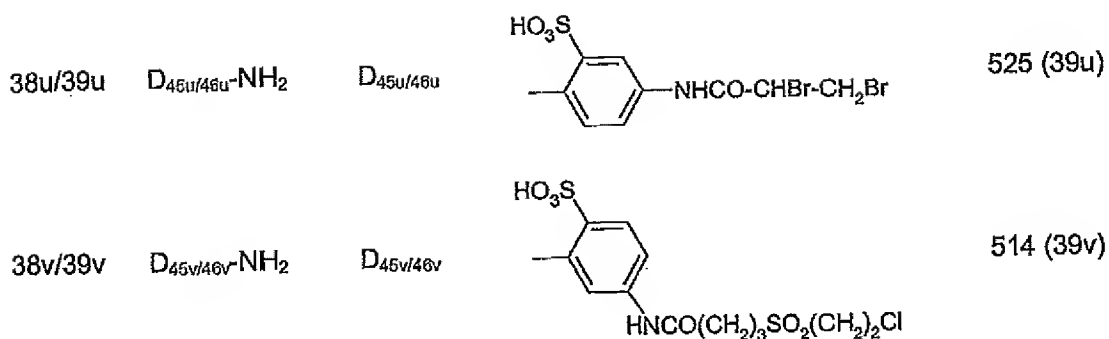
- 44 -

38f/39f	D _{45f/46f} -NH ₂	D _{45f/46f}		524 (39f)
38g/39g	D _{45g/46g} -NH ₂	D _{45g/46g}		520 (39g)
38h/39h	D _{45h/46h} -NH ₂	D _{45h/46h}		518 (39h)
38i/39i	D _{45i/46i} -NH ₂	D _{45i/46i}		520 (39i)
38j/39j	D _{45j/46j} -NH ₂	D _{45j/46j}		528 (39j)
38k/39k	D _{45k/46k} -NH ₂	D _{45k/46k}		518 (39k)
38l/39l	D _{45l/46l} -NH ₂	D _{45l/46l}		522 (39l)
38m/39m	D _{45m/46m} -NH ₂	D _{45m/46m}		520 (39m)

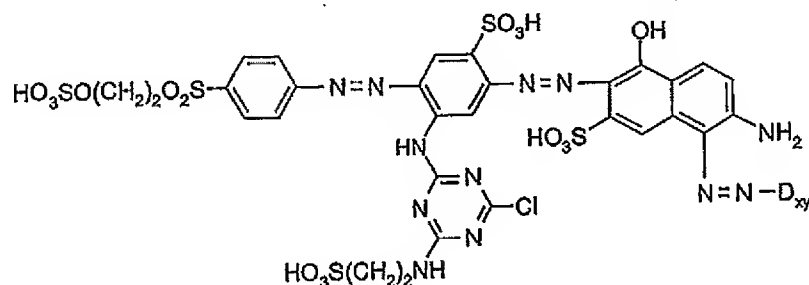
- 45 -

38n/39n	D _{46n/46n} -NH ₂	D _{45n/46n}		510 (39n)
38o/39o	D _{45o/46o} -NH ₂	D _{45o/46o}		508 (39o)
38p/39p	D _{45p/46p} -NH ₂	D _{45p/46p}		512 (39p)
38q/39q	D _{45q/46q} -NH ₂	D _{45q/46q}		525 (39q)
38r/39r	D _{45r/46r} -NH ₂	D _{45r/46r}		520 (39r)
38s/39s	D _{45s/46s} -NH ₂	D _{45s/46s}		519 (39s)
38t/39t	D _{45t/46t} -NH ₂	D _{45t/46t}		508 (39t)

- 46 -



Examples 40 to 57: By proceeding as described in Example 21 but, Instead of using the acid suspension of the diazo compound of the amine of formula $D_{10}-NH_2$, using an equimolar amount of the diazo compound of an amine of formula $D_{xy}-NH_2$, a dye of formula



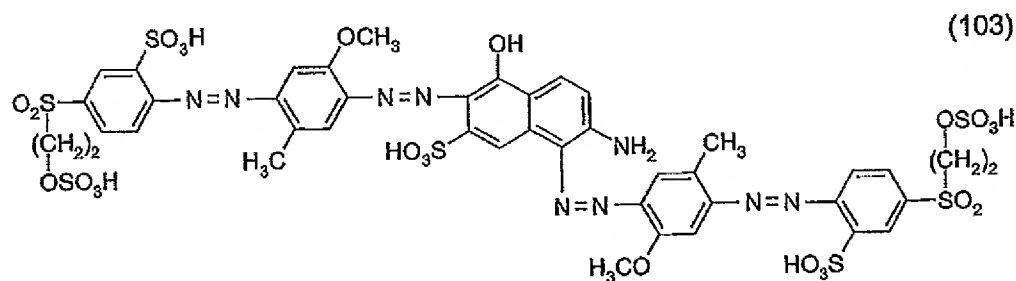
is obtained wherein D_{xy} corresponds to one of the radicals listed in Table 3, the definitions given in Table 1 applying to that radical. The dyes dye wool and cellulose in bluish violet shades having good allround fastness properties.

Table 3:

Ex.	D_{xy}	Ex.	D_{xy}	Ex.	D_{xy}
40	D_{11}	46	D_{17}	52	D_{23}
41	D_{12}	47	D_{18}	53	D_{24}
42	D_{13}	48	D_{19}	54	D_{25}
43	D_{14}	49	D_{20}	55	D_{26}
44	D_{15}	50	D_{21}	56	D_{27}
45	D_{16}	51	D_{22}	57	D_{28}

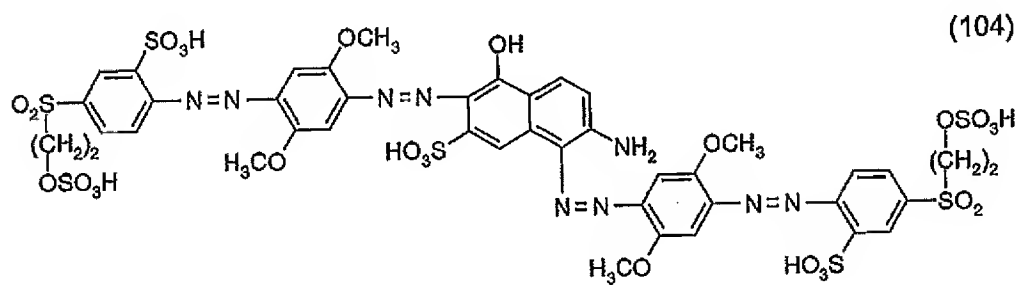
Examples 58 to 62: The compounds of the following formulae can be prepared analogously to the procedure described in Example 21

58



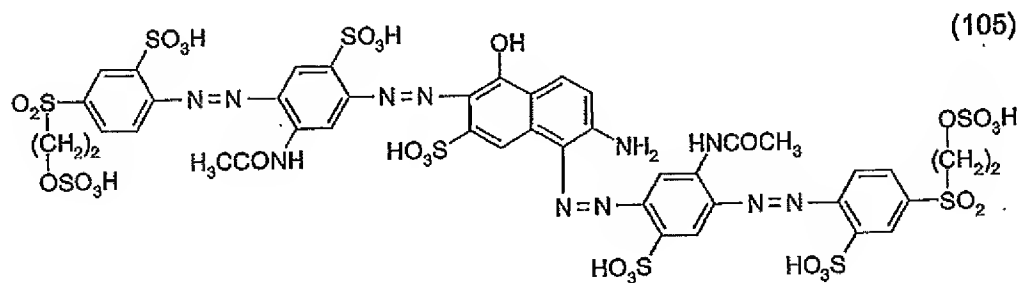
(λ_{max} : 588 nm)

59



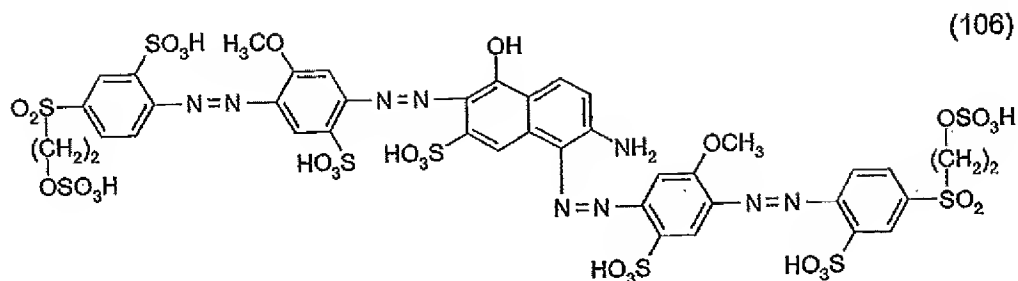
(λ_{max} : 604 nm)

60



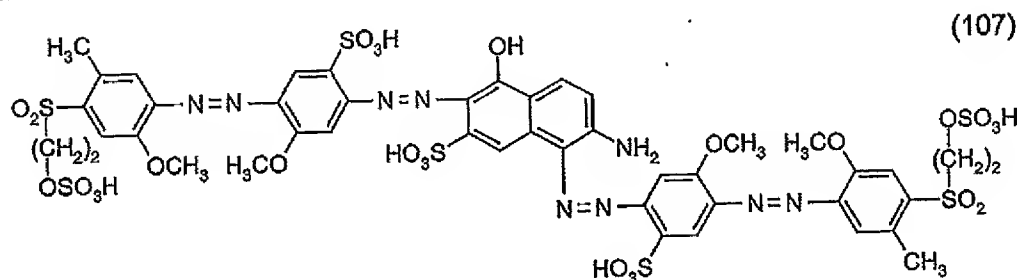
(λ_{max} : 554 nm)

61

(λ_{\max} : 555 nm)

and

62



which dye wool and cellulose in violet to dark-blue shades having good allround fastness properties.

Dyeing procedure I

100 parts of cotton fabric are introduced at 60°C into 1500 parts of a dye bath containing 45 g/l of sodium chloride and 2 parts of the reactive dye obtained according to Example 21. After 45 minutes at 60°C, 20 g/l of calcined soda are added. Dyeing is continued for a further 45 minutes at that temperature. The dyed goods are then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

As an alternative to the above procedure, the dyeing can be carried out at 80°C instead of at 60°C.

Dyeing procedure II

0.1 part of the dye according to Example 21 is dissolved in 200 parts of water, and 0.5 part of sodium sulfate, 0.1 part of a levelling agent (based on the condensation product of a higher

aliphatic amine and ethylene oxide) and also 0.5 part of sodium acetate are added. The pH is then adjusted to a value of 5.5 using acetic acid (80 %). The dye bath is heated at 50°C for 10 minutes and then 10 parts of a woollen fabric are added. Heating is then carried out in the course of approximately 50 minutes to a temperature of 100°C and dyeing is carried out at that temperature for 60 minutes, after which the dye bath is allowed to cool and the dyed goods are removed. The woollen fabric is washed with hot and cold water, and is then spun and dried.

Printing procedure I

3 parts of the dye obtained according to Example 21 are sprinkled, with rapid stirring, into 100 parts of a stock thickener containing 50 parts of 5 % sodium alginate thickener, 27.8 parts of water, 20 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 1.2 parts of sodium hydrogen carbonate. The print paste so obtained is used to print a cotton fabric, and the resulting printed material is dried and steamed in saturated steam for 2 minutes at 102°C. The printed fabric is then rinsed, if desired soaped at the boil and rinsed again, and subsequently dried.

Printing procedure II

(a) Mercerised cotton satin is pad-dyed with a liquor containing 30 g/l of sodium carbonate and 50 g/l of urea (70 % liquor pick-up) and dried.

(b) Using a drop-on-demand inkjet head (bubble jet), the cotton satin pretreated according to Step (a) is printed with an aqueous ink containing

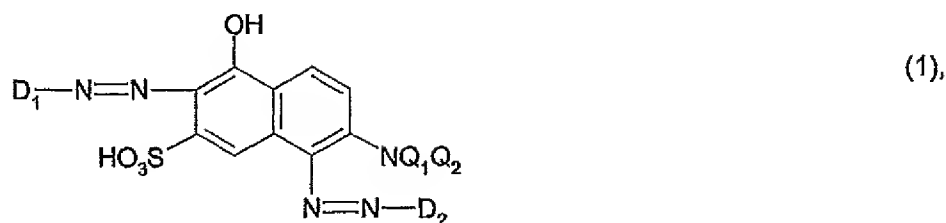
- 10 % by weight of the reactive dye according to Example 21,
- 20 % by weight of 1,2-propylene glycol and
- 70 % by weight of water.

The print is dried completely and fixed in saturated steam for 8 minutes at 102°C, cold-rinsed, washed off at the boil, rinsed again and dried.

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What is claimed is:

1. A reactive dye of formula

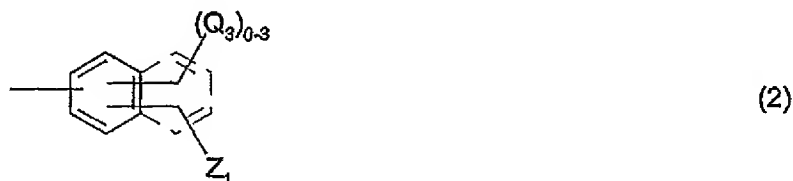


wherein

Q₁ and Q₂ are each independently of the other hydrogen or unsubstituted or substituted C₁-C₄alkyl,

D₁ is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye,

D₂ has the same definition as D₁ or is a radical of formula



wherein

(Q₃)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄alkyl, C₁-C₄alkoxy, carboxy and sulfo and

Z₁ is a radical of formula

-SO₂-Y . (3a),

-NH-CO-(CH₂)_m-SO₂-Y (3b),

-CONH-(CH₂)_n-SO₂-Y (3c),

-NH-CO-CH(Hal)-CH₂-Hal (3d) or

-NH-CO-C(Hal)=CH₂ (3e),

Y is vinyl or a -CH₂-CH₂-U radical and U is a group that is removable under alkaline conditions,

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m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen,

with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

2. A reactive dye according to claim 1, wherein

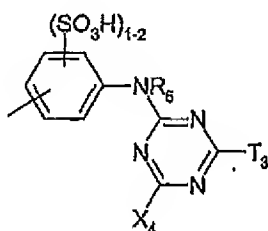
Q₁ and Q₂ are hydrogen.

3. A reactive dye according to either claim 1 or claim 2, wherein

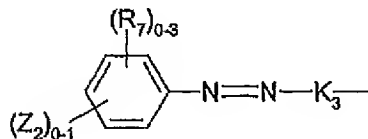
Y is -Cl, -Br, -F, -OSO₃H, -SSO₃H, -OCO-CH₃, -OPO₃H₂, -OCO-C₆H₅, -OSO₂-C₁-C₄alkyl or -OSO₂-N(C₁-C₄alkyl)₂.

4. A reactive dye according to any one of claims 1 to 3, wherein

D₁ corresponds to a radical of formula (5) or (11)



(5) or



(11),

wherein

R₅ is hydrogen or C₁-C₄alkyl,

(R₇)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen,

C₁-C₄alkyl, C₁-C₄alkoxy, C₂-C₄alkanoylamino, carboxy and sulfo,

X₄ is fluorine or chlorine,

Z₂ is a fibre-reactive radical of formula

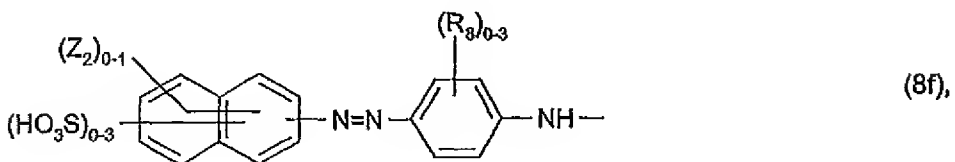
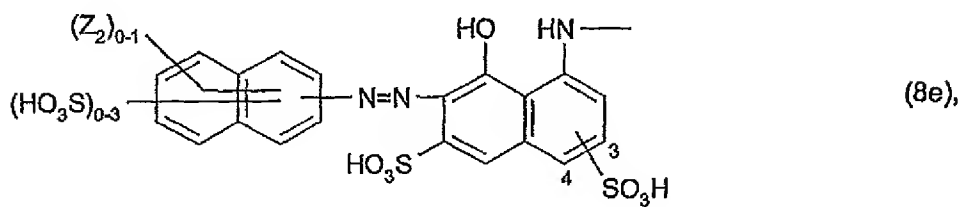
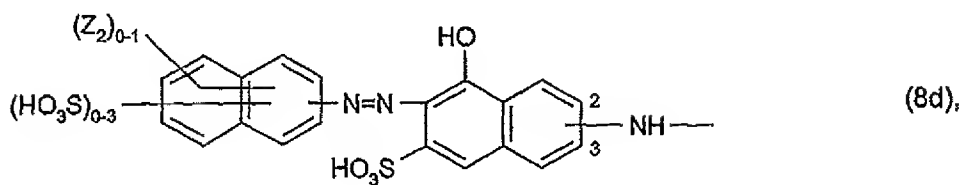
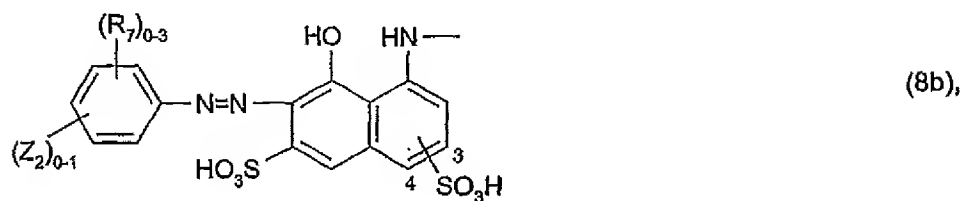
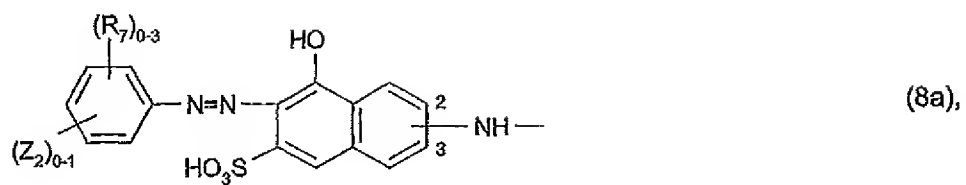


(3a),

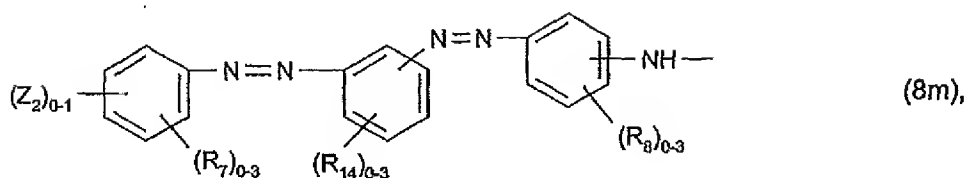
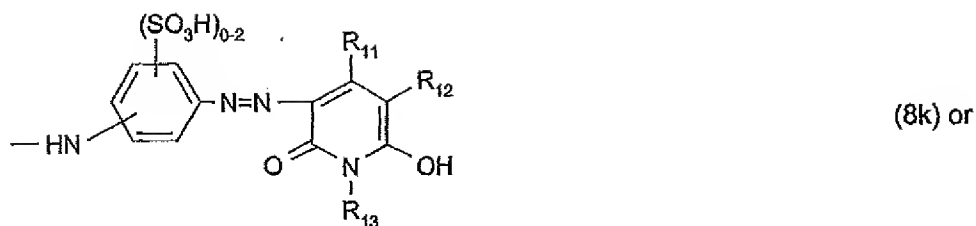
wherein

Y is vinyl or β -sulfoethyl,

T₃ is a radical of formula



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wherein

$(R_7)_{0-3}$ is as defined hereinabove,

$(R_8)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl; C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy; amino, C_2 - C_4 alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C_1 - C_4 alkyl/sulfonylamino and sulfo,

R_{11} and R_{13} are each independently of the other hydrogen, C_1 - C_4 alkyl or phenyl,

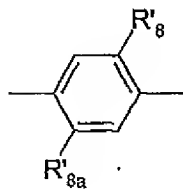
R_{12} is hydrogen, cyano, carbamoyl or sulfomethyl,

$(R_{14})_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl,

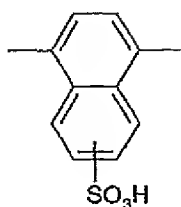
C_1 - C_4 alkoxy, halogen, carboxy and sulfo, and

Z_2 is as defined hereinabove,

K_3 is the radical of a coupling component of formula



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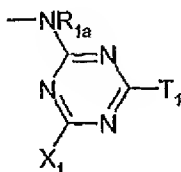


(12b),

wherein

R'_8 is hydrogen, sulfo, or C_1 - C_4 alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido or a radical of formula



(3f),

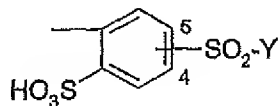
wherein

R_{1a} is hydrogen,

T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted in the same way on the phenyl ring and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and X_1 is chlorine.

5. A reactive dye according to any one of claims 1 to 4, wherein

D_2 is a radical of formula.



(2aa),

wherein

Y is vinyl or β -sulfatoethyl.

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6. A process for the preparation of a dye of formula (1) according to claim 1, which comprises

(i) diazotisation of approximately one molar equivalent of an amine of formula



in customary manner and reaction with approximately one molar equivalent of a compound of formula



to form a compound of formula



and

(ii) diazotisation of approximately one molar equivalent of an amine of formula



in customary manner and reaction with approximately one molar equivalent of the compound of formula (15a) obtained according to (i) to form a compound of formula (1) according to claim 1 wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions and preferred meanings given in claim 1.

7. The use of a reactive dye according to any one of claims 1 to 5 or a reactive dye prepared according to claim 6 in the dyeing or printing of hydroxy-group-containing or nitrogen-containing fibre material.

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8. Use according to claim 7, wherein cellulosic fibre material, especially cotton-containing fibre material, is dyed or printed.
9. An aqueous ink that comprises a reactive dye of formula (1) according to claim 1.
10. A process for printing textile fibre material, paper or plastics film according to the inkjet printing method, which comprises using an aqueous ink according to claim 9.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/051044

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B62/09 C09B62/513 C09B62/475

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 011 140 A (PATSCHE MANFRED ET AL) 4 January 2000 (2000-01-04) example 35	1,5-8
Y	DE 196 40 189 A (BASF AG) 2 April 1998 (1998-04-02) examples 10.1-10.7	1-10
Y	JP 63 199269 A (NIPPON KAYAKU CO LTD) 17 August 1988 (1988-08-17) the whole document	1-10
Y	US 6 537 332 B1 (TZIKAS ATHANASSIOS ET AL) 25 March 2003 (2003-03-25) the whole document	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

Date of the actual completion of the international search

24 August 2005

Date of mailing of the international search report

31/08/2005

Name and mailing address of the ISA

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Authorized officer

Friebe, F

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/051044

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6011140	A	04-01-2000	DE 19600765 A1 AU 1309697 A DE 69707835 D1 DE 69707835 T2 WO 9725377 A1 EP 0876431 A1 JP 2000503058 T	17-07-1997 01-08-1997 06-12-2001 11-04-2002 17-07-1997 11-11-1998 14-03-2000
DE 19640189	A	02-04-1998	DE 19640189 A1 CN 1239493 A ,C DE 59708079 D1 WO 9814522 A1 EP 0929610 A1 JP 2001501242 T US 6197941 B1	02-04-1998 22-12-1999 02-10-2002 09-04-1998 21-07-1999 30-01-2001 06-03-2001
JP 63199269	A	17-08-1988	JP 1987232 C JP 7013200 B	08-11-1995 15-02-1995
US 6537332	B1	25-03-2003	AT 247694 T AU 4911099 A DE 59906709 D1 WO 0006652 A2 EP 1137716 A2 ES 2205850 T3 JP 2002521548 T PT 1137716 T	15-09-2003 21-02-2000 25-09-2003 10-02-2000 04-10-2001 01-05-2004 16-07-2002 30-01-2004

THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.:	Not Assigned	§
		§
Applicants:	Tzikas et al.	§
		§
Examiner:	Not Assigned	§
		§
Art Unit:	Not Assigned	§
		§
Title:	Fibre-Reactive Dyes, Their	§
	Preparation and Their Use	§

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

PRELIMINARY AMENDMENT UNDER 37 C.F.R. § 1.115

Dear Sir:

Submitted herewith is a Preliminary Amendment under 37 C.F.R. § 1.115. Please amend the application as follows:

Amendments to the Specification begin on page 2 of this paper.

Amendments to the Claims are reflected in the listing of claims which begins on page 3 of this paper.

Remarks/Arguments begin on page 13 of this paper.

Amendments to the Specification

At the top of the first page, just under the title, insert:

Cross Reference to Related Applications

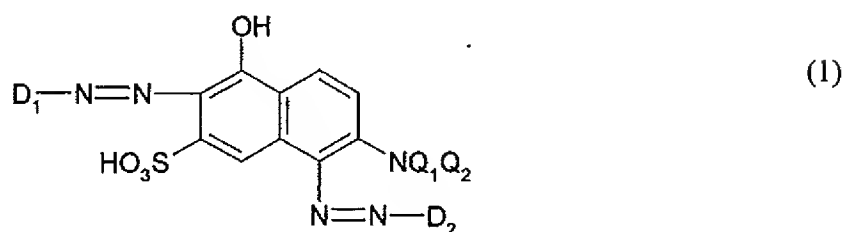
- - This application is the National Phase of International Application PCT/EP2005/051044 filed March 9, 2005 which designated the U.S. and which claims priority to European Pat. App. No. 04101144.6 filed March 19, 2004. The noted applications are incorporated herein by reference. - -

Amendments to the Claims

This listing of claims will replace all prior versions, and listings, of claims in the application:

Listing of Claims:

Claim 1 (original). A reactive dye of formula

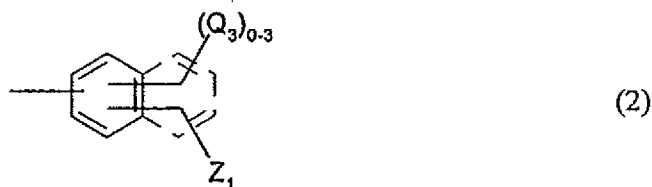


wherein

Q_1 and Q_2 are each independently of the other hydrogen or unsubstituted or substituted C_1 - C_4 alkyl,

D_1 is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye,

D_2 has the same definition as D_1 or is a radical of formula



wherein

$(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, carboxy and sulfo and

Z₁ is a radical of formula



Y is vinyl or a $-\text{CH}_2-\text{CH}_2-\text{U}$ radical and U is a group that is removable under alkaline conditions,

m and n are each independently of the other the number 2, 3 or 4, and Hal is halogen, with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

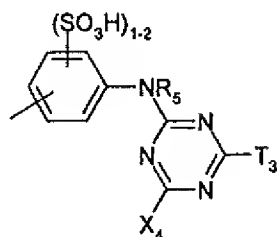
Claim 2 (original). A reactive dye according to claim 1, wherein Q₁ and Q₂ are hydrogen.

Claim 3 (currently amended). A reactive dye according to ~~either~~ claim 1 ~~or claim 2~~, wherein

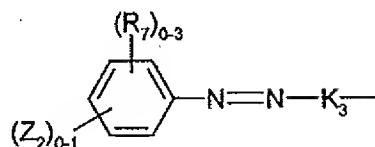
Y is $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{H}$, $-\text{SSO}_3\text{H}$, $-\text{OCO}-\text{CH}_3$, $-\text{OPO}_3\text{H}_2$, $-\text{OCO}-\text{C}_6\text{H}_5$, $-\text{OSO}_2-\text{C}_1-\text{C}_4$ alkyl or $-\text{OSO}_2-\text{N}(\text{C}_1-\text{C}_4 \text{ alkyl})_2$.

Claim 4 (currently amended). A reactive dye according to claim 1 ~~any one of claims 1 to 3~~, wherein

D₁ corresponds to a radical of formula (5) or (11)



(5) or



(11),

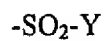
wherein

R_5 is hydrogen or C_1 - C_4 alkyl,

$(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy and sulfo,

X_4 is fluorine or chlorine,

Z_2 is a fibre-reactive radical of formula

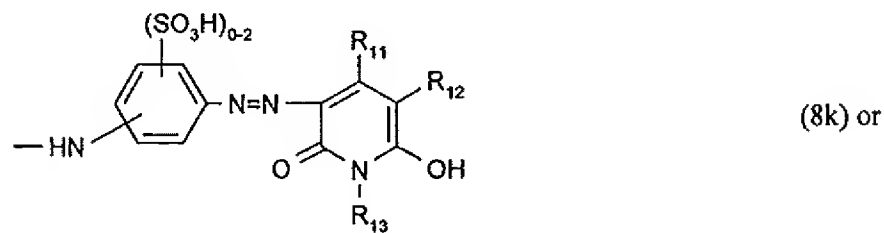
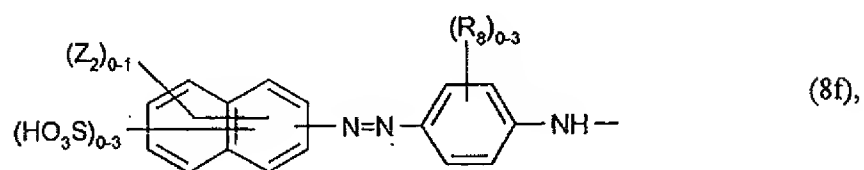
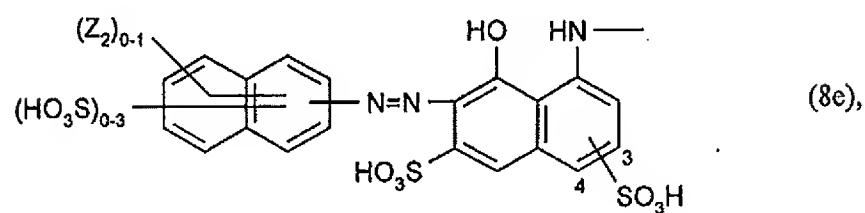
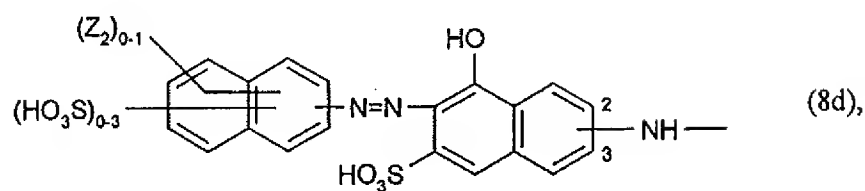
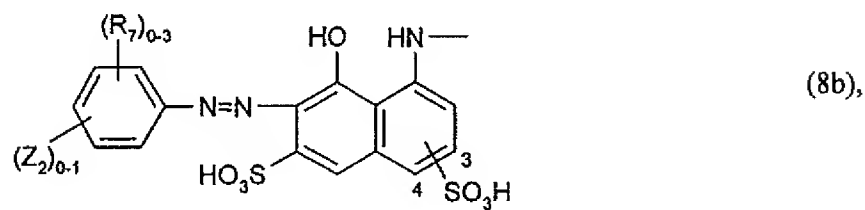
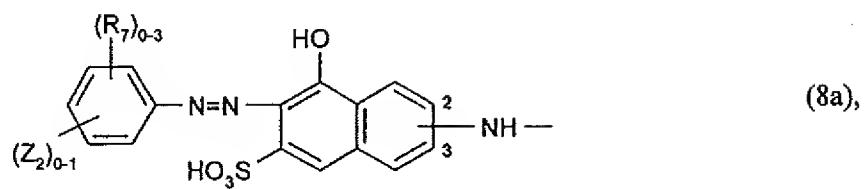


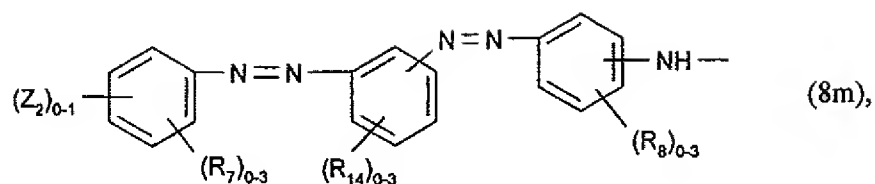
(3a),

wherein

Y is vinyl or β -sulfatoethyl,

T_3 is a radical of formula





wherein

(R₇)₀₋₃ is as defined hereinabove,

(R₈)₀₋₃ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C₁-C₄ alkyl; C₁-C₄ alkoxy unsubstituted or substituted by hydroxy, sulfato or by C₁-C₄ alkoxy; amino, C₂-C₄ alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C₁-C₄ alkylsulfonylamino and sulfo,

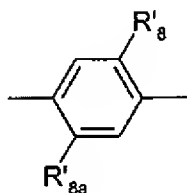
R₁₁ and R₁₃ are each independently of the other hydrogen, C₁-C₄ alkyl or phenyl,

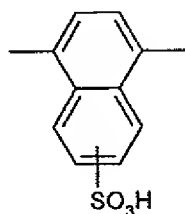
R₁₂ is hydrogen, cyano, carbamoyl or sulfomethyl,

(R₁₄)₀₋₃ denotes from 0 to 3 identical or different substituents from the group C₁-C₄ alkyl, C₁-C₄ alkoxy, halogen, carboxy and sulfo, and

Z₂ is as defined hereinabove,

K₃ is the radical of a coupling component of formula



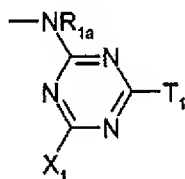


(12b),

wherein

R'₈ is hydrogen, sulfo, or C₁-C₄ alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, ureido or a radical of formula



(3f),

wherein

R_{1a} is hydrogen,

T₁ is amino; N-mono- or N,N-di-C₁-C₄ alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N-C₁-C₄ alkyl-N-phenylamino unsubstituted or substituted in the same way on the phenyl ring and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X₁ is chlorine.

Claim 5 (currently amended). A reactive dye according to claim 1 ~~any one of claims 1 to 4~~, wherein

D₂ is a radical of formula



wherein

Y is vinyl or β-sulfatoethyl.

Claim 6 (currently amended). A process for the preparation of a dye of formula (1) according to claim 1, which comprises

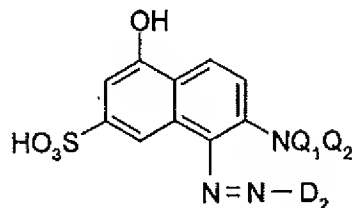
(i) diazotisation of approximately one molar equivalent of an amine of formula



~~in customary manner~~ and reaction with approximately one molar equivalent of a compound of formula



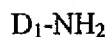
to form a compound of formula



(15a);

and

(ii) diazotisation of approximately one molar equivalent of an amine of formula



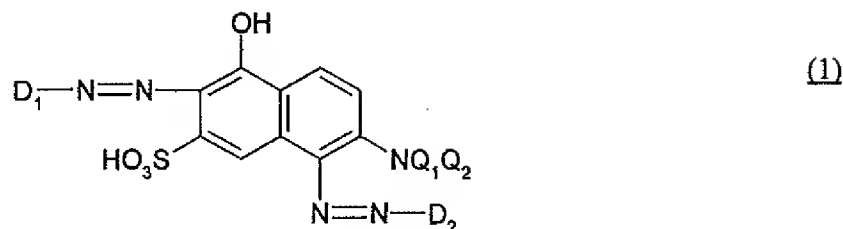
(16)

~~in customary manner~~ and reaction with approximately one molar equivalent of the compound of formula (15a) obtained according to (i) to form a compound of formula (1) according to claim 1 wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions ~~and preferred meanings~~ given in claim 1.

Claims 7-8 (canceled).

Claim 9 (original). An aqueous ink that comprises a reactive dye of formula (1) according to claim 1.

Claim 10 (currently amended). A process for printing a substrate ~~textile fibre material, paper or plastics film according to the inkjet printing method, which comprises using an aqueous ink according to claim 9 comprising spraying individual droplets of an aqueous ink onto the substrate from a nozzle in a controlled manner wherein the aqueous ink comprises a reactive dye of formula~~

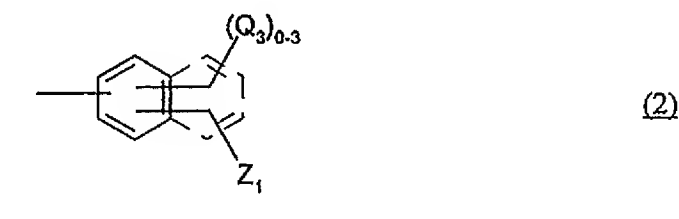


wherein

Q₁ and Q₂ are each independently of the other hydrogen or unsubstituted or substituted C₁-C₄alkyl.

D₁ is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye.

D₂ has the same definition as D₁ or is a radical of formula

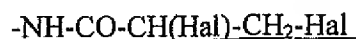


wherein

(Q₃)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄alkyl, C₁-C₄alkoxy, carboxy and sulfo and

Z₁ is a radical of formula





(3d) or



(3e).

Y is vinyl or a -CH₂-CH₂-U radical and U is a group that is removable under alkaline conditions.

m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen,

with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

Claim 11 (new). The process of claim 10 wherein the substrate is selected from textile fibre material, paper and plastic film.

Claim 12 (new). A method for dyeing fibre material which comprises applying a reactive dye of formula (1) according to claim 1 to the fibre material and fixing the reactive dye to the fibre material.

Claim 13 (new). The method according to claim 12 wherein the fibre material is a hydroxyl-group-containing fibre material or a nitrogen-group-containing fibre material.

Claim 14 (new). The method of claim 12 wherein the fibre material is a cellulosic fibre material.

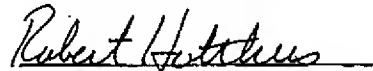
Claim 15 (new). The method of claim 14 wherein the cellulosic fibre material is a cotton-containing fibre material.

Remarks

Currently pending in the present application are claims 1-6 and 9-15. Claims 7 and 8 have been canceled without prejudice. No new matter has been added.

Should any fee be due in connection with the filing of this document, the Commissioner for Patents is hereby authorized to deduct said fee from Huntsman Corporation Deposit Account No. 08-3442.

Respectfully Submitted,



Robert Holthus

Reg. No. 50,347

Attorney for Applicants

Date: 9/15/06

THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.:	10/592,976	§
		§
Applicants:	Tzikas et al.	§
		§
Filed:	09/15/2006	§
		§
Examiner:	Elhilo	§
		§
Art Unit:	1796	§
		§
Title:	Fibre-Reactive Dyes, Their	§
	Preparation and Their Use	§

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO OFFICE COMMUNICATION MAILED DECEMBER 16, 2008

Dear Sir:

Applicants submit this response to the Office Communication mailed December 16, 2008. In view of the following amendments and remarks, Applicants request reconsideration and withdrawal of the outstanding rejections, and allowance of the claims pending in this application.

Amendments to the Claims begin on page 2 of this paper.

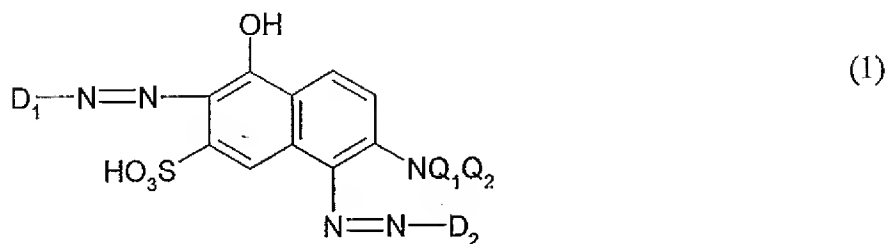
Remarks/Arguments begin on page 16 of this paper.

Amendments to the Claims

This listing of claims will replace all prior versions, and listings, of claims in the application:

Listing of Claims:

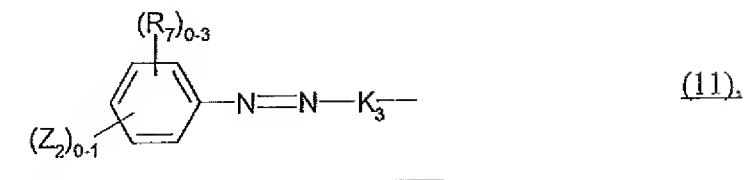
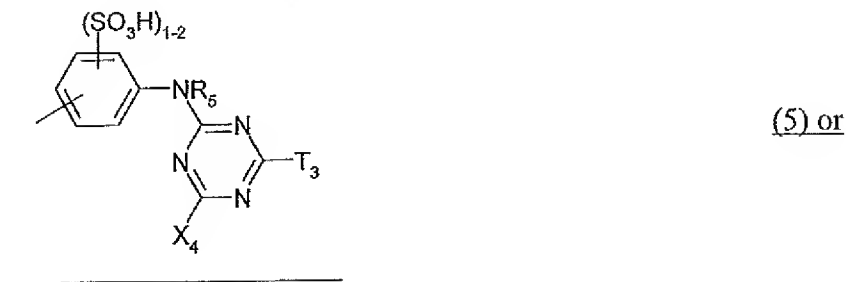
Claim 1 (currently amended). A reactive dye of formula



wherein

Q₁ and Q₂ are each independently of the other hydrogen or unsubstituted or substituted C₁-C₄ alkyl,

D₁ corresponds to a radical of formula (5) or (11)



wherein

R₅ is hydrogen or C₁-C₄ alkyl.

(R₇)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, carboxy and sulfo,

X₄ is fluorine or chlorine.

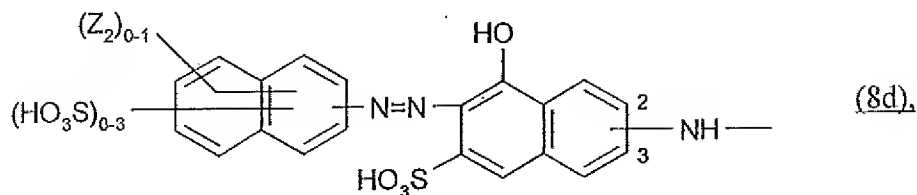
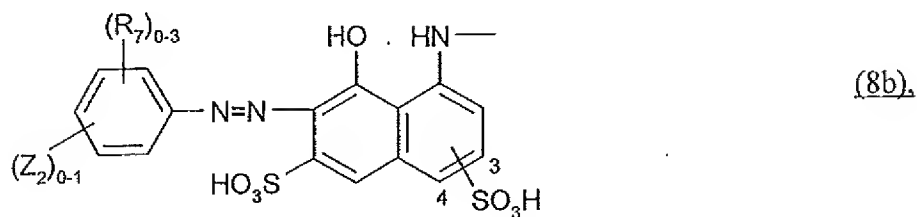
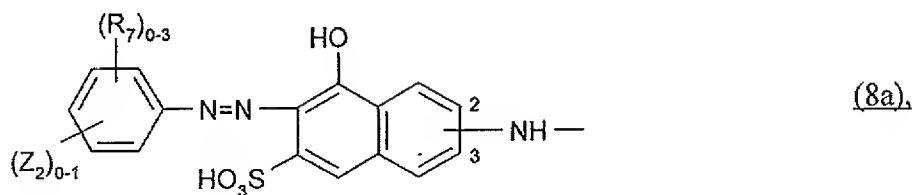
Z₂ is a fibre-reactive radical of formula

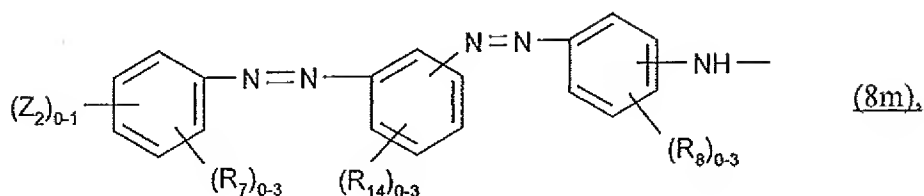
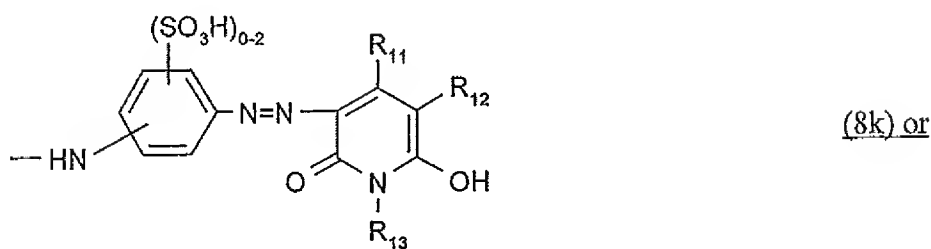
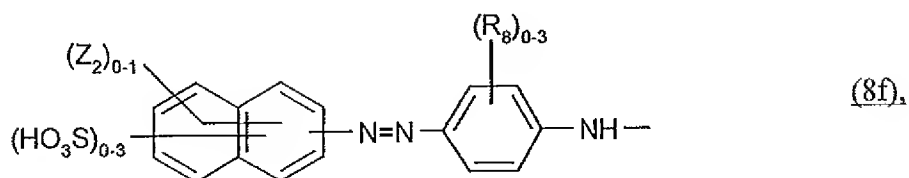
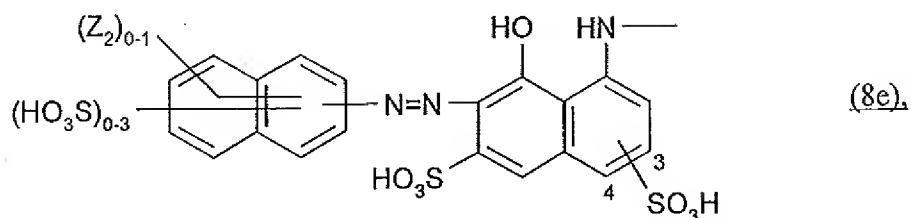


wherein

Y is vinyl or β -sulfatoethyl,

T₃ is a radical of formula





wherein

$(R_7)_{0-3}$ is as defined hereinabove,

$(R_8)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy, amino, C_2 - C_4 alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C_1 - C_4 alkylsulfonylamino and sulfo,

R₁₁ and R₁₃ are each independently of the other hydrogen, C₁-C₄ alkyl or phenyl,

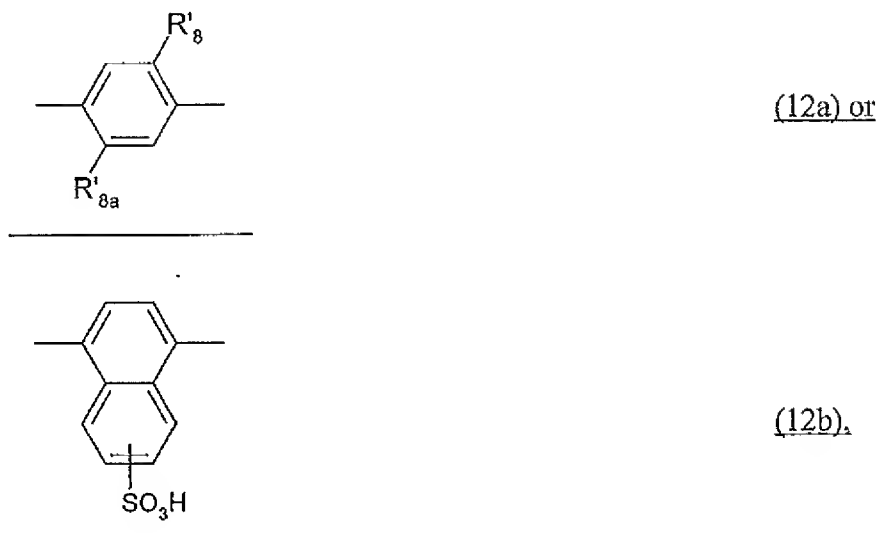
R₁₂ is hydrogen, cyano, carbamoyl or sulfomethyl,

(R₁₄)₀₋₃ denotes from 0 to 3 identical or different substituents from the group C₁-C₄ alkyl,

C₁-C₄ alkoxy, halogen, carboxy and sulfo, and

Z₂ is as defined hereinabove,

K₃ is the radical of a coupling component of formula



wherein

R'₈ is hydrogen, sulfo, or C₁-C₄ alkoxy unsubstituted or substituted in the alkyl moiety by

hydroxy or by sulfato, and

R'_{8a} is hydrogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, ureido or a radical of
formula



wherein

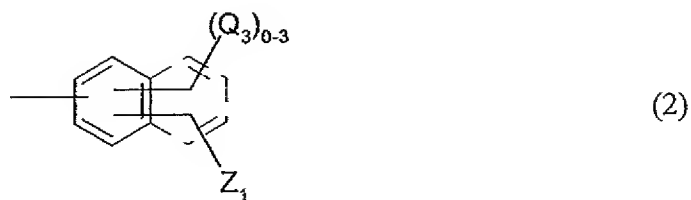
R_{1a} is hydrogen,

T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted in the same way on the phenyl ring and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X_1 is chlorine

is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye,

D_2 has the same definition as D_1 or is a radical of formula



wherein

(Q₃)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group
halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, carboxy and sulfo and

Z₁ is a radical of formula



Y is vinyl or a -CH₂-CH₂-U radical and U is a group that is removable under alkaline conditions,

m and n are each independently of the other the number 2, 3 or 4, and Hal is halogen,
with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

Claim 2 (original). A reactive dye according to claim 1, wherein Q₁ and Q₂ are hydrogen.

Claim 3 and 4 (cancelled). A reactive dye according to claim 1 wherein

≠ U is -Cl, -Br, -F, -OSO₃H, -SSO₃H, -OCO-CH₃, -OPO₃H₂, -OCO-C₆H₅, -OSO₂-C₁-C₄ alkyl or -OSO₂-N(C₁-C₄ alkyl)₂.

Claim 4 (cancelled).

Claim 5 (previously presented). A reactive dye according to claim 1 wherein D₂ is a radical of formula



wherein

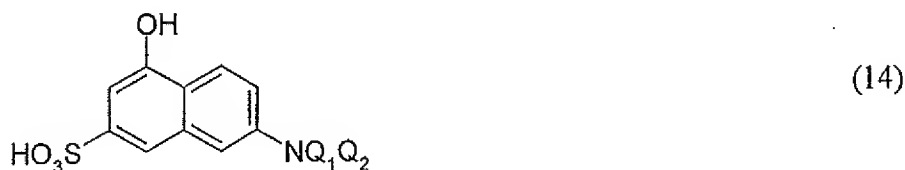
Y is vinyl or β -sulfoethyl.

Claim 6 (previously presented). A process for the preparation of a dye of formula (1) according to claim 1, which comprises

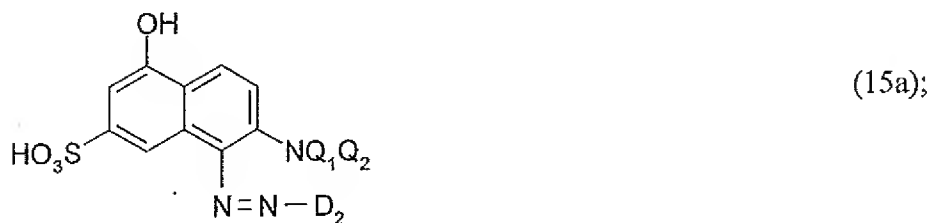
(i) diazotisation of approximately one molar equivalent of an amine of formula



and reaction with approximately one molar equivalent of a compound of formula



to form a compound of formula



and

(ii) diazotisation of approximately one molar equivalent of an amine of formula

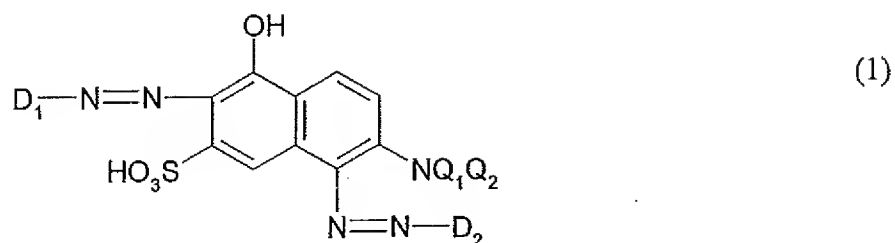


and reaction with approximately one molar equivalent of the compound of formula (15a) obtained according to (i) to form a compound of formula (1) according to claim 1 wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions given in claim 1.

Claims 7-8 (canceled).

Claim 9 (original). An aqueous ink that comprises a reactive dye of formula (1) according to claim 1.

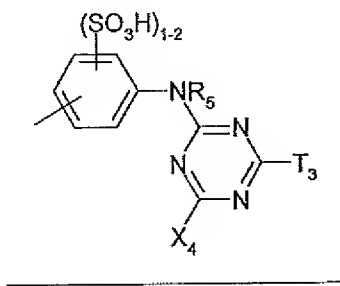
Claim 10 (currently amended). A process for printing a substrate comprising spraying individual droplets of an aqueous ink onto the substrate from a nozzle in a controlled manner wherein the aqueous ink comprises a reactive dye of formula



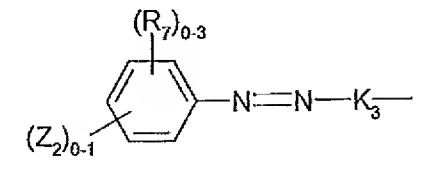
wherein

Q_1 and Q_2 are each independently of the other hydrogen or unsubstituted or substituted C_1 - C_4 alkyl,

D_1 corresponds to a radical of formula (5) or (11)



(5) or



(11).

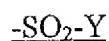
wherein

R_5 is hydrogen or C_1 - C_4 alkyl.

$(\text{R}_7)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy and sulfo.

X_4 is fluorine or chlorine.

Z_2 is a fibre-reactive radical of formula

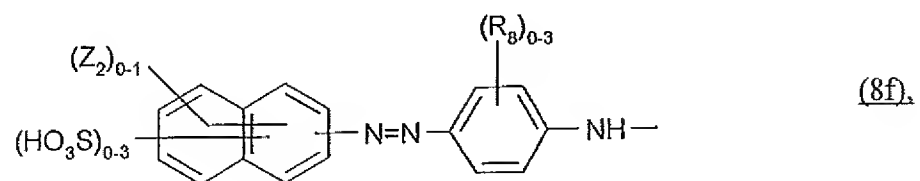
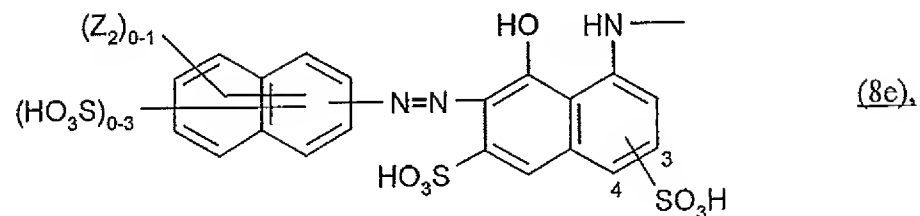
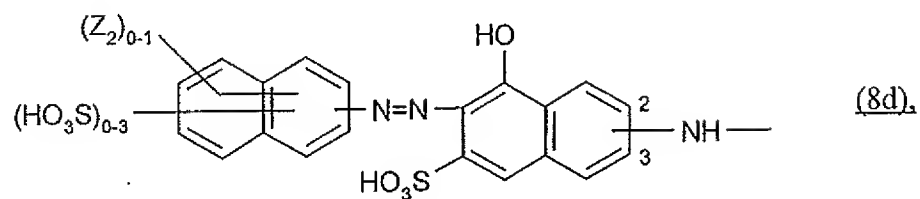
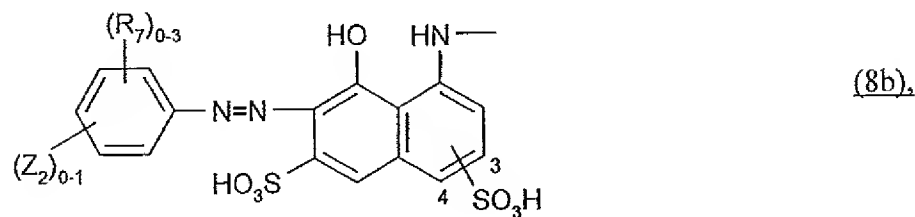
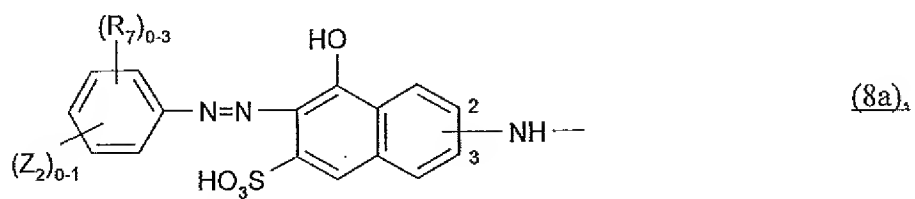


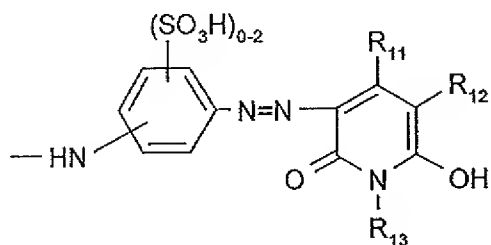
(3a).

wherein

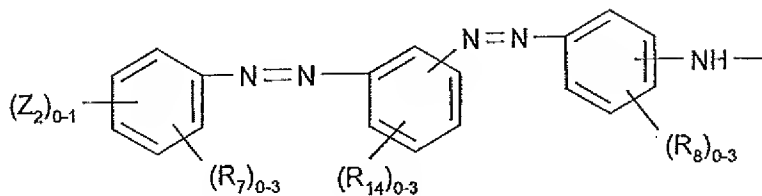
Y is vinyl or β -sulfatoethyl.

T_3 is a radical of formula





(8k) or



(8m).

wherein

(R₇)₀₋₃ is as defined hereinabove.

(R₈)₀₋₃ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C₁-C₄ alkyl, C₁-C₄ alkoxy unsubstituted or substituted by hydroxy, sulfato or by C₁-C₄ alkoxy, amino, C₂-C₄ alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C₁-C₄ alkylsulfonylamino and sulfo.

R₁₁ and R₁₃ are each independently of the other hydrogen, C₁-C₄ alkyl or phenyl.

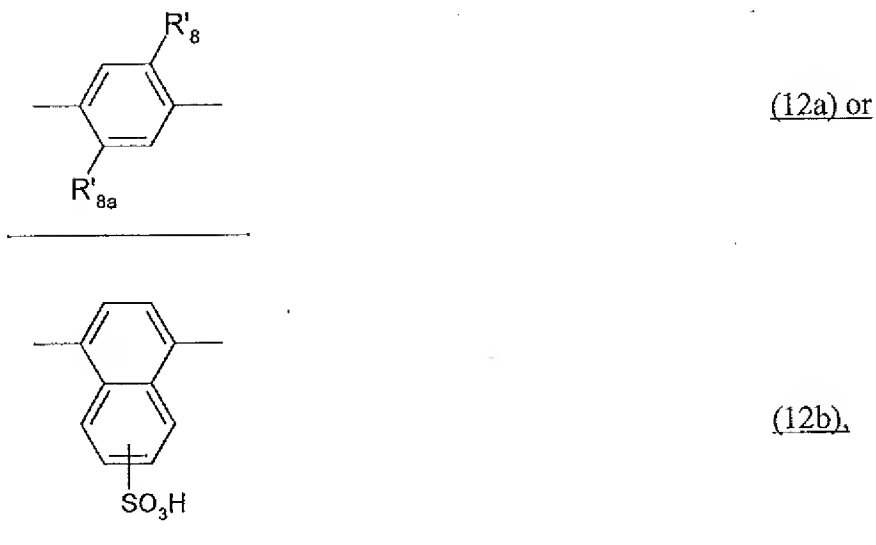
R₁₂ is hydrogen, cyano, carbamoyl or sulfomethyl.

(R₁₄)₀₋₃ denotes from 0 to 3 identical or different substituents from the group C₁-C₄ alkyl,

C₁-C₄ alkoxy, halogen, carboxy and sulfo, and

Z₂ is as defined hereinabove.

K₃ is the radical of a coupling component of formula



wherein

R'_8 is hydrogen, sulfo, or C₁-C₄ alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, ureido or a radical of formula



wherein

R_{1a} is hydrogen,

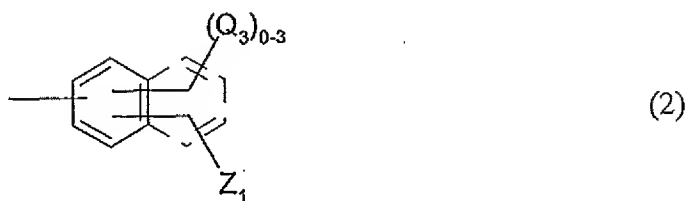
T₁ is amino; N-mono- or N,N-di-C₁-C₄ alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N-C₁-C₄ alkyl-N-phenylamino unsubstituted or substituted in

the same way on the phenyl ring and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X₁ is chlorine

~~is the radical of a diazo component, which is itself a mono or dis-azo dye or contains such a dye,~~

D₂ has the same definition as D₁ or is a radical of formula



wherein

(Q₃)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄alkyl, C₁-C₄alkoxy, carboxy and sulfo and

Z₁ is a radical of formula

-SO₂-Y (3a),

-NH-CO-(CH₂)_m-SO₂-Y (3b),

-CONH-(CH₂)_n-SO₂-Y (3c),

-NH-CO-CH(Hal)-CH₂-Hal (3d) or

-NH-CO-C(Hal)=CH₂ (3e),

Y is vinyl or a $-\text{CH}_2-\text{CH}_2-\text{U}$ radical and U is a group that is removable under alkaline conditions,

m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen,

with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

Claim 11 (previously presented). The process of claim 10 wherein the substrate is selected from textile fibre material, paper and plastic film.

Claim 12 (previously presented). A method for dyeing fibre material which comprises applying a reactive dye of formula (1) according to claim 1 to the fibre material and fixing the reactive dye to the fibre material.

Claim 13 (previously presented). The method according to claim 12 wherein the fibre material is a hydroxyl-group-containing fibre material or a nitrogen-group-containing fibre material.

Claim 14 (previously presented). The method of claim 12 wherein the fibre material is a cellulosic fibre material.

Claim 15 (previously presented). The method of claim 14 wherein the cellulosic fibre material is a cotton-containing fibre material.

Remarks

Currently pending in the present application are claims 1-3, 5-6 and 9-15. Claims 1 and 10 have been amended to include the limitations of claim 4; thus, claim 4 has been canceled without prejudice. Claim 3 has been amended by replacing "Y" with "U". Support for this amendment can be found at, for example, page 3, paragraph 7. No new matter has been added. In view of the above amendments and following remarks, Applicants respectfully request reconsideration by the Examiner, and advancement of the application to allowance.

Allowable Subject Matter

The Examiner has indicated claim 4 would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. Applicants would like to thank the Examiner for this allowance.

Claims 1 and 10 have been amended to include the limitations of claim 4. Therefore, Applicants respectfully submit these claims, and all claims depending on these claims are now allowable.

35 U.S.C. § 112

The Examiner rejected claims 1, 3 and 10 under 35 U.S.C. § 112, second paragraph as being indefinite. Claims 1 and 10 have been amended to clearly define D₁. In addition, claim 3 has been amended by replacing "Y" with "U". Accordingly, Applicants respectfully request the rejections under 35 U.S.C. § 112, second paragraph, be withdrawn.

35 U.S.C. §§ 102/103

The Examiner rejected claims 1, 2, 5 and 6 as being anticipated by Tzikas et al. (US 6,537,332). The Examiner also rejected claims 9-15 as being obvious over Tzikas et al.

As noted above, claims 1 and 10 have been amended to include the limitations of claim 4. Applicants respectfully request these rejections are moot.

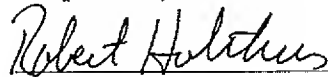
Double Patenting

The Examiner provisionally rejected claims 1, 2, 9 and 12 on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1, 4, 7 and 10 of Application No. 10/551,319. In view of the above amendment to claim 1 and 10, Applicants respectfully submit this rejection is moot.

Should any fee be due in connection with the filing of this document, the Commissioner for Patents is hereby authorized to deduct said fee from Huntsman Corporation Deposit Account No. 08-3442.

Huntsman Corporation
10003 Woodloch Forest Drive
The Woodlands, TX 77380
(281) 719-4553

Respectfully Submitted,



Robert Holthus
Reg. No. 50,347
Attorney for Applicants

Date: 3/16/09



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NOTICE OF ALLOWANCE AND FEE(S) DUE

7590

04/06/2009

Legal Department
Huntsman Corporation
10003 Woodloch Forest Drive
The Woodlands, TX 77380

EXAMINER	
ELH/LQ, EISA B	
ART UNIT	PAPER NUMBER

1796

DATE MAILED: 04/06/2009

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/592,976	09/15/2006	Athanasios Tzikas	423032	4055
TITLE OF INVENTION: FIBRE-REACTIVE DYES, THEIR PREPARATION AND THEIR USE				

APPLN. TYPE	SMALL ENTITY	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	NO	\$1510	\$300	\$0	\$1810	07/06/2009

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. **PROSECUTION ON THE MERITS IS CLOSED.** THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN **THREE MONTHS** FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. **THIS STATUTORY PERIOD CANNOT BE EXTENDED.** SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the SMALL ENTITY status shown above.

If the SMALL ENTITY is shown as YES, verify your current SMALL ENTITY status:

A. If the status is the same, pay the TOTAL FEE(S) DUE shown above.

B. If the status above is to be removed, check box 5b on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and twice the amount of the ISSUE FEE shown above, or

If the SMALL ENTITY is shown as NO:

A. Pay TOTAL FEE(S) DUE shown above, or

B. If applicant claimed SMALL ENTITY status before, or is now claiming SMALL ENTITY status, check box 5a on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and 1/2 the ISSUE FEE shown above.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: **Mail** Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

7590

04/06/2009

Legal Department
Huntsman Corporation
10003 Woodloch Forest Drive
The Woodlands, TX 77380

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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10/592,976

09/15/2006

Athanassios Tzikas

423032

4055

TITLE OF INVENTION: FIBRE-REACTIVE DYES, THEIR PREPARATION AND THEIR USE

APPLN. TYPE	SMALL ENTITY	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
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nonprovisional

NO

\$1510

\$300

\$0

\$1810

07/06/2009

EXAMINER	ART UNIT	CLASS-SUBCLASS
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ELHILO, EISA B

1796

008-641000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

- ☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. Use of a Customer Number is required.

2. For printing on the patent front page, list

- (1) the names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1	_____
2	_____
3	_____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☐ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:

- ☐ Issue Fee
☐ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): (Please first reapply any previously paid issue fee shown above)

- ☐ A check is enclosed.
☐ Payment by credit card. Form PTO-2038 is attached.
☐ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. Change in Entity Status (from status indicated above)

- ☐ a. Applicant claims SMALL ENTITY status. See 37 CFR 1.27. ☐ b. Applicant is no longer claiming SMALL ENTITY status. See 37 CFR 1.27(g)(2).

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature _____

Date _____

Typed or printed name _____

Registration No. _____

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/592,976	09/15/2006	Athanassios Tzikas	423032	4055
7590 04/06/2009				
Legal Department Huntsman Corporation 10003 Woodloch Forest Drive The Woodlands, TX 77380				
			EXAMINER ELHILO, EISA B	
			ART UNIT 1796	PAPER NUMBER
DATE MAILED: 04/06/2009				

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (application filed on or after May 29, 2000)

The Patent Term Adjustment to date is 393 day(s). If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the Patent Term Adjustment will be 393 day(s).

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (<http://pair.uspto.gov>).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

Notice of Allowability	Application No.	Applicant(s)	
	10/592,976	TZIKAS ET AL.	
	Examiner	Art Unit	
	Eisa B. Elhilo	1796	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to the amendment filed on March 16, 2009.
2. ☒ The allowed claim(s) is/are 1-3,5,6 and 9-15.
3. ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
 - a) ☒ All b) ☐ Some* c) ☐ None of the:
 1. ☒ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. _____.
 3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

4. ☐ A SUBSTITUTE OATH OR DECLARATION must be submitted. Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL PATENT APPLICATION (PTO-152) which gives reason(s) why the oath or declaration is deficient.
5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
 - (a) ☐ Including changes required by the Notice of Draftsperson's Patent Drawing Review (PTO-948) attached
 - 1) ☐ hereto or 2) ☐ to Paper No./Mail Date _____.
 - (b) ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

- | | |
|---|---|
| <ol style="list-style-type: none"> 1. <input type="checkbox"/> Notice of References Cited (PTO-892) 2. <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) 3. <input type="checkbox"/> Information Disclosure Statements (PTO/SB/08),
Paper No./Mail Date _____ 4. <input type="checkbox"/> Examiner's Comment Regarding Requirement for Deposit
of Biological Material | <ol style="list-style-type: none"> 5. <input type="checkbox"/> Notice of Informal Patent Application 6. <input type="checkbox"/> Interview Summary (PTO-413),
Paper No./Mail Date _____ 7. <input checked="" type="checkbox"/> Examiner's Amendment/Comment 8. <input checked="" type="checkbox"/> Examiner's Statement of Reasons for Allowance 9. <input type="checkbox"/> Other _____ |
|---|---|

/Eisa B Elhilo/
 Primary Examiner, Art Unit 1796
 April 2, 2009

DETAILED ACTION

- 1 This action is responsive to the amendment filed on March 16, 2009.
- 2 The cancellation of claim 4 is acknowledged. Pending claims are 1-3, 5-6 and 9-15.
- 3 All the previous rejections are withdrawn because of the applicant's amendment.

EXAMINER'S AMENDMENT

- 4 An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

The application has been amended as follows:

In the claims:

In claim 3, in line 1, replace "and 4 (cancelled)" with -- (currently amended) --.

- 5 Claims 1-3, 5-6 and 9-15 are allowed.

STATEMENT OF REASONS FOR ALLOWANCE

- 6 The following is an examiner's statement of reasons for allowance:

The closest prior art of record ((US 6,537,332 B1) teaches and discloses a dye compound having a formula (1) in which both D_1 and D_2 represent a radical of a formula (2) (see col. 1, lines 35-60). However, the closest prior art of record (US' 332 B1) does not teach or disclose the dye compounds of the claimed formula (1), in which D_1 corresponds to a radical of the formula (5) or (11) as required in the recent amended claims. Further, the closest prior art of record (US' 332 B1) does not teach or disclose an aqueous ink, a process for printing a substrate or a method for dyeing fiber materials comprising or utilizing a reactive dye of the claimed formula (1), in

which D₁ corresponds to a radical of the formula (5) or (11) as required in the recent amended claims. Accordingly, the claimed subject matter as a whole would not have been obvious to one having ordinary skill in the art of fiber materials dyeing formulation.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Eisa B. Elhilo whose telephone number is (571) 272-1315. The examiner can normally be reached on M - F (8:00 -4:30).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Pyon Harold can be reached on (571) 272-1498. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

Application/Control Number: 10/592,976
Art Unit: 1796

Page 4

/Eisa B Elhilo/
Primary Examiner, Art Unit 1796
April 2, 2009



US007572301B2

(12) **United States Patent**
Tzikas et al.

(10) Patent No.: **US 7,572,301 B2**
(45) Date of Patent: **Aug. 11, 2009**

(54) **FIBRE-REACTIVE DYES, THEIR PREPARATION AND THEIR USE**

(75) Inventors: Athanassios Tzikas, Pratteln (CH);
Georg Roentgen, Freiburg (DE);
Hubert Jean Luc Christnachner,
Dietwiller (FR)

(73) Assignee: **Huntsman International LLC, The**
Woodlands, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 393 days.

(21) Appl. No.: **10/592,976**

(22) PCT Filed: **Mar. 9, 2005**

(86) PCT No.: **PCT/EP2005/051044**

§ 371 (c)(1),
(2), (4) Date: **Sep. 15, 2006**

(87) PCT Pub. No.: **WO2005/090484**

PCT Pub. Date: **Sep. 29, 2005**

(65) **Prior Publication Data**

US 2008/0250575 A1 Oct. 16, 2008

(30) **Foreign Application Priority Data**

Mar. 19, 2004 (EP) 04101144

(51) Int. Cl.
C09B 67/00 (2006.01)
C09B 62/00 (2006.01)

(52) U.S. Cl. 8/641; 8/667; 8/669; 8/670;
8/681; 8/688; 534/637

(58) Field of Classification Search 8/641,
8/667, 669, 670, 681, 688; 534/637
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,011,140 A 1/2000 Zamponi et al.
6,197,941 B1 3/2001 Zamponi et al.
6,537,332 B1 * 3/2003 Tzikas et al. 8/549

FOREIGN PATENT DOCUMENTS

DE 19640189 4/1998
JP 63199269 8/1988

OTHER PUBLICATIONS

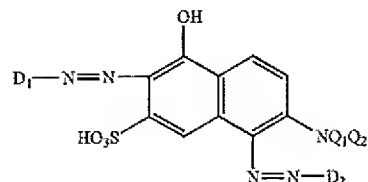
STIC Search Report dated Dec. 1, 2008.*

* cited by examiner

Primary Examiner—Eisa B Elhilo

(57) **ABSTRACT**

Reactive dyes of formula



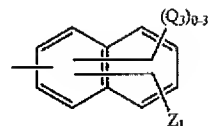
(1)

wherein

Q₁ and Q₂ are each independently of the other hydrogen or unsubstituted or substituted C₁-C₄alkyl,

D₁ is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye,

D₂ has the same definition as D₁ or is a radical of formula



(2)

wherein

(Q₂)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄alkyl, C₁-C₄alkoxy, carboxy and sulfo and

Z₁ is a radical of formula

—SO₂—Y (3a),

—NH—CO—(CH₂)_m—SO₂—Y (3b),

—CONH—(CH₂)_n—SO₂—Y (3c),

—NH—CO—CH(Hal)—CH₂—Hal (3d) or

—NH—CO—C(Hal)—CH₂ (3e),

Y is vinyl or a —CH₂—CH₂—U radical and U is a group that is removable under alkaline conditions,
m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen,
are suitable for dyeing cellulosic or amide-group-containing fibre materials.

12 Claims, No Drawings

1

FIBRE-REACTIVE DYES, THEIR
PREPARATION AND THEIR USE

The present invention relates to fibre-reactive dyes, to a process for their preparation and to their use in the dyeing or printing of textile fibre materials.

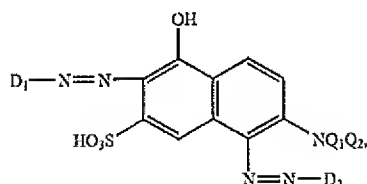
The practice of dyeing using reactive dyes has recently led to higher demands being made on the quality of the dyeings and the economic efficiency of the dyeing process. As a result, there continues to be a need for novel reactive dyes having improved properties, especially in respect of their application.

Dyeing nowadays requires reactive dyes that have sufficient substantivity and at the same time have good ease of washing off of unfixed dye. They should also have a good colour yield and high reactivity, the objective being to provide especially dyeings having high degrees of fixing. The known dyes do not satisfy these requirements in all properties.

The problem underlying the present invention is accordingly to find, for the dyeing and printing of fibre materials, novel improved reactive dyes having the qualities characterised above to a high degree. The novel dyes should especially be distinguished by high fixing yields and high fibre-dye bond stabilities, and in addition it should be possible for dye not fixed to the fibre to be washed off readily. The dyes should also yield dyeings having good allround fastness properties, for example fastness to light and to wetting.

It has been found that the problem posed is largely solved by the novel dyes defined herein-below.

The present invention therefore relates to reactive dyes of formula

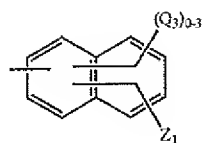


wherein

Q_1 and Q_2 are each independently of the other hydrogen or unsubstituted or substituted C_1 - C_4 alkyl,

D_1 is the radical of a diazo component, which is itself a mono- or dis-azo dye or contains such a dye,

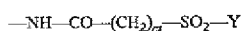
D_2 has the same definition as D_1 or is a radical of formula



wherein

$(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, carboxy and sulfo and

Z_1 is a radical of formula



2



Y is vinyl or a $-\text{CH}_2-\text{CH}_2-\text{U}$ radical and U is a group that is removable under alkaline conditions,

m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen,

with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

As C_1 - C_4 alkyl there come into consideration for Q_1 , Q_2 and Q_3 , each independently of the others, for example, methyl, ethyl, n -propyl, isopropyl, n -butyl, sec -butyl, isobutyl and $tert$ -butyl, especially methyl and ethyl. The alkyl radicals Q_1 and Q_2 may be unsubstituted or may be substituted, for example, by hydroxy, sulfo, sulfo, cyano, carboxy, C_1 - C_4 alkoxy or by phenyl, preferably by hydroxy, sulfo, C_1 - C_4 alkoxy or by phenyl. The corresponding unsubstituted radicals are preferred.

Preferably, one of the radicals Q_1 and Q_2 is hydrogen and the other of the radicals Q_1 and Q_2 is one of the above-mentioned unsubstituted or substituted C_1 - C_4 alkyl radicals.

Q_1 and Q_2 are especially preferably hydrogen.

As C_1 - C_4 alkoxy there come into consideration for Q_3 , for example, methoxy, ethoxy, n -propoxy, isopropoxy, n -butoxy, isobutoxy and $tert$ -butoxy, preferably methoxy and ethoxy and especially methoxy.

As halogen there come into consideration for Q_3 , for example, fluorine, chlorine, bromine and iodine, preferably chlorine and bromine and especially chlorine.

Preferably, $(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy and sulfo, especially methyl, methoxy and sulfo.

Hal is, for example, chlorine or bromine, especially bromine.

As leaving group U there come into consideration, for example, $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{H}$, $-\text{SSO}_3\text{H}$, $-\text{OCO}-\text{CH}_3$, $-\text{OPO}_3\text{H}_2$, $-\text{OCO}-\text{C}_6\text{H}_5$, $-\text{OSO}_2-\text{C}_1-\text{C}_4\text{alkyl}$ and $-\text{OSO}_2-\text{N}(\text{C}_1-\text{C}_4\text{alkyl})_2$. U is preferably a group of formula $-\text{Cl}$, $-\text{OSO}_3\text{H}$, $-\text{SSO}_3\text{H}$, $-\text{OCO}-\text{CH}_3$, $-\text{OCO}-\text{C}_6\text{H}_5$ or $-\text{OPO}_3\text{H}_2$, especially $-\text{Cl}$ or $-\text{OSO}_3\text{H}$ and more especially $-\text{OSO}_3\text{H}$.

Examples of suitable radicals Y are accordingly vinyl, β -bromo- or β -chloro-ethyl, β -acetoxy-ethyl, β -benzoyloxy-ethyl, β -phosphatoethyl, β -sulfatoethyl and β -thiosulfatoethyl.

Preferably, Y is independently vinyl, β -chloroethyl or β -sulfatoethyl, especially vinyl or β -sulfatoethyl.

m and n are preferably each independently of the other the number 2 or 3.

m is especially preferably the number 3.

n is especially preferably the number 2.

Preferably, Z_1 is a radical of formula (3a), (3b) or (3c), especially of formula (3a) or (3c) and more especially of formula (3a), the variables having the definitions and preferred meanings given hereinabove.

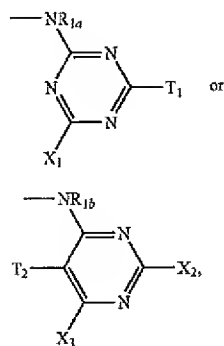
As substituents of the radical D_1 there come into consideration the substituents customary for azo dyes. The examples which follow may be mentioned: C_1 - C_4 alkyl, which is understood to include methyl, ethyl, n - and iso -propyl and n -, iso -, sec - and $tert$ -butyl; C_1 - C_4 alkoxy, which is understood to include methoxy, ethoxy, n - and iso -propoxy and n -, iso -, sec - and $tert$ -butoxy; hydroxy- C_1 - C_4 alkoxy; phenoxy; C_2 - C_6 alkanoylamino unsubstituted or substituted in the alkyl moiety by hydroxy or by C_1 - C_4 alkoxy, such as, for example, acetylamino, hydroxyacetyl-amino, methoxyacetylamino or

propionylamino; benzoylamino unsubstituted or substituted in the phenyl moiety by hydroxy, sulfo, halogen, C₁-C₄alkyl or by C₁-C₄alkoxy; C₁-C₆alkoxy-carbonylamino unsubstituted or substituted in the alkyl moiety by hydroxy, C₁-C₄alkyl or by C₁-C₄alkoxy; phenoxy-carbonylamino unsubstituted or substituted in the phenyl moiety by hydroxy, C₁-C₄alkyl or by C₁-C₄alkoxy; amino; N-C₁-C₄alkyl- or N,N-di-C₁-C₄alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, C₁-C₄alkoxy, carboxy, cyano, halogen, sulfo, sulfato, phenyl or by sulfophenyl, such as, for example, methylamino, ethylamino, N,N-dimethylamino, N,N-diethylamino, β-cyanoethylamino, β-hydroxyethylamino, N,N-di-β-hydroxyethylamino, β-sulfoethylamino, γ-sulfo-n-propylamino, β-sulfato-ethylamino, N-ethyl-N-(3-sulfobenzyl)amino, N-(β-sulfoethyl)-N-benzylamino; cyclohexylamino; N-phenylamino or N-C₁-C₄alkyl-N-phenylamino unsubstituted or substituted in the phenyl moiety by nitro, C₁-C₄alkyl, C₁-C₄alkoxy, carboxy, halogen or by sulfo; C₁-C₄-alkoxycarbonyl, for example methoxy- or ethoxy-carbonyl; trifluoromethyl; nitro; cyano; halogen, which is generally understood to include, for example, fluorine, bromine and especially chlorine; ureido; hydroxy; carboxy; sulfo; sulfomethyl; carbamoyl; carbamido; sulfamoyl; N-phenylsulfamoyl or N-C₁-C₄alkyl-N-phenylsulfamoyl unsubstituted or substituted in the phenyl moiety by sulfo or by carboxy; methyl- or ethyl-sulfonyl; and C₁-C₄alkylsulfonylamino.

Fibre-reactive radicals are also suitable as substituents of the radical D₁.

Fibre-reactive radicals, such as, for example, the above-mentioned radicals of formulae (3a) to (3e), are to be understood as being those which are capable of reacting with the hydroxy groups of cellulose, with the amino, carboxy, hydroxy and thiol groups in wool and silk or with the amino groups and, possibly, with the carboxy groups of synthetic polyamides, to form covalent chemical bonds. The fibre-reactive radicals are generally bonded to the dye radical directly or by way of a bridging member. Suitable fibre-reactive radicals are, for example, those which contain at least one removable substituent at an aliphatic, aromatic or heterocyclic radical or in which the said radicals contain a radical suitable for reaction with the fibre material, for example a vinyl radical.

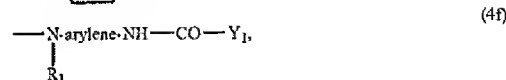
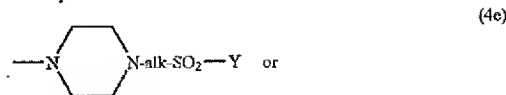
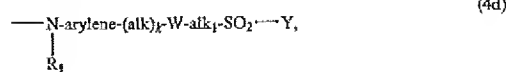
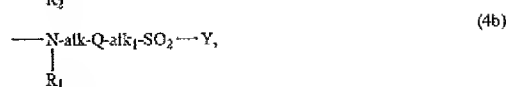
A fibre-reactive radical present in D₁ corresponds, for example, to the above formula (3a), (3b), (3c), (3d) or (3e) or to the formula



wherein

X₁ is halogen, 3-carboxypyridin-1-yl or 3-carbamoylpyridin-1-yl,

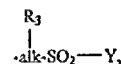
T₁ independently has the same definition as X₁, is a non-fibre-reactive substituent or is a fibre-reactive radical of formula



wherein

R₁, R_{1a} and R_{1b} are each independently of the others hydrogen or C₁-C₄alkyl,

R₂ is hydrogen, C₁-C₄alkyl unsubstituted or substituted by hydroxy, sulfo, sulfato, carboxy or by cyano, or a radical



R₃ is hydrogen, hydroxy, sulfo, sulfato, carboxy, cyano, halogen, C₁-C₄alkoxycarbonyl, C₁-C₄alkanoyloxy, carbamoyl or the group ---SO₂---Y,

alk and alk₁ are each independently of the other linear or branched C₁-C₆alkylene,

arylene is a phenylene or naphthylene radical unsubstituted or substituted by sulfo, carboxy, C₁-C₄alkyl, C₁-C₄alkoxy or by halogen,

Q is an ---O--- or ---NR₁--- radical wherein R₁ is as defined above,

W is a ---SO₂---NR₂---, ---CONR₂--- or ---NR₂CO--- group, wherein R₂ is as defined above,

Y has the definition and preferred meanings given herein above,

Y₁ is a ---CH(Hal)---CH₂---Hal or ---C(Hal)=CH₂ group and Hal has the definition and preferred meanings given herein above,

k is the number 0 or 1,

X₂ is halogen or C₁-C₄alkylsulfonyl,

X₃ is halogen or C₁-C₄alkyl and

T₂ is hydrogen, cyano or halogen.

R₁, R_{1a} and R_{1b} are each independently of the others preferably hydrogen, methyl or ethyl and especially hydrogen.

R₂ is preferably hydrogen or C₁-C₄alkyl, such as, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl and especially hydrogen, methyl or ethyl. Especially preferably, R₂ is hydrogen.

R₃ is preferably hydrogen.

When T_1 is a non-fibre-reactive substituent it may be, for example, hydroxy; C_1 - C_4 alkoxy; C_1 - C_4 alkylthio unsubstituted or substituted, for example, by hydroxy, carboxy or by sulfo; amino; amino mono- or di-substituted by C_1 - C_8 alkyl, wherein the alkyl may itself be substituted, for example, by sulfo, sulfato, hydroxy, carboxy or by phenyl, especially by sulfo or by hydroxy, and may be interrupted one or more times by the radical $-O-$; cyclohexylamino; morpholino; N - C_1 - C_4 alkyl- N -phenylamino, phenylamino or naphthylamino, wherein the phenyl or naphthyl is unsubstituted or substituted, for example, by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy, sulfo or by halogen and the alkyl is unsubstituted or substituted, for example, by hydroxy, sulfo or by sulfato.

Examples of suitable non-fibre-reactive substituents T_1 are amino, methylamino, ethylamino, β -hydroxyethylamino, N -methyl- N - β -hydroxyethylamino, N -ethyl- N - β -hydroxyethylamino, N,N -di- β -hydroxyethylamino, β -sulfoethylamino, cyclohexylamino, morpholino, 2-, 3- or 4-chlorophenylamino, 2-, 3- or 4-methylphenylamino, 2-, 3- or 4-methoxyphenylamino, 2-, 3- or 4-sulfophenylamino, 2,5-disulfophenylamino, 2-, 3- or 4-carboxyphenylamino, 1- or 2-naphthylamino, 1-sulfo-2-naphthylamino, 4,8-disulfo-2-naphthylamino, N -ethyl- N -phenylamino, N -methyl- N -phenylamino, methoxy, ethoxy, n - or iso-propoxy and hydroxy.

As a non-fibre-reactive substituent, T_1 is preferably C_1 - C_4 alkoxy; C_1 - C_4 alkylthio unsubstituted or substituted by hydroxy, carboxy or by sulfo; hydroxy; amino; N -mono- or N,N -di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N - C_1 - C_4 alkyl- N -phenylamino unsubstituted or substituted on the phenyl ring in the same way as phenylamino and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups.

Especially preferred non-fibre-reactive substituents T_1 are amino, N -methylamino, N -ethylamino, N - β -hydroxyethylamino, N -methyl- N - β -hydroxyethylamino, N -ethyl- N - β -hydroxyethylamino, N,N -di- β -hydroxyethylamino, β -sulfoethylamino, morpholino, 2-, 3- or 4-carboxyphenylamino, 2-, 3- or 4-sulfophenylamino, 2,5-disulfophenylamino and N - C_1 - C_4 alkyl- N -phenylamino.

X_1 is preferably halogen, for example fluorine, chlorine or bromine and especially preferably chlorine or fluorine.

T_2 , X_2 and X_3 as halogen are, for example, fluorine, chlorine or bromine, especially chlorine or fluorine.

X_2 as C_1 - C_4 alkylsulfonyl is, for example, ethylsulfonyl or methylsulfonyl and especially methylsulfonyl.

X_3 as C_1 - C_4 alkyl is, for example, methyl, ethyl, n - or isopropyl or n -, iso- or tert-butyl and especially methyl.

X_2 and X_3 are preferably each independently of the other chlorine or fluorine.

T_2 is preferably cyano or chlorine.

alk and alk₁ are each independently of the other, for example, a methylene, ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene or 1,6-hexylene radical or a branched isomer thereof.

Preferably, alk and alk₁ are each independently of the other a C_1 - C_4 alkylene radical and especially preferably an ethylene radical or propylene radical.

arylene is preferably an unsubstituted or, for example, sulfo-, methyl-, methoxy- or carboxy-substituted 1,3- or 1,4-phenylene radical, and especially preferably an unsubstituted 1,3- or 1,4-phenylene radical.

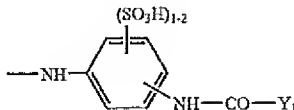
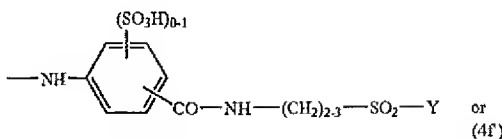
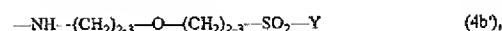
Q is preferably $-NH-$ or $-O-$ and especially preferably $-O-$.

W is preferably a group of formula $-CONH-$ or $-NHCO-$, especially a group of formula $-CONH-$.

k is preferably the number 0.

The reactive radicals of formulae (4a) to (4f) are preferably such radicals in which W is a group of formula $-CONH-$, R_1 is hydrogen, methyl or ethyl, R_2 and R_3 are each hydrogen, Q is the radical $-O-$ or $-NH-$, alk and alk₁ are each independently of the other ethylene or propylene, arylene is phenylene unsubstituted or substituted by methyl, methoxy, carboxy or by sulfo, Y is vinyl or β -sulfoethyl, Y_1 is $-CHBr-CH_2Br$ or $-CBr=CH_2$ and k is the number 0.

A fibre-reactive radical present in D_1 preferably corresponds to a radical of the above formula (3a), (3b), (3c), (3d), (3e) or (3f), wherein Y is vinyl, β -chloroethyl or β -sulfoethyl, Hal is bromine, R_{1a} is hydrogen, m and n are each independently of the other the number 2 or 3, X_1 is halogen, T_1 is C_1 - C_4 alkoxy; C_1 - C_4 alkylthio; hydroxy; amino; N -mono- or N,N -di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino or N - C_1 - C_4 alkyl- N -phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy, and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, or T_1 is a fibre-reactive radical of formula



especially (4c') or (4d'), wherein

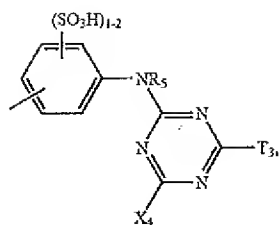
$(R_4)_{0,2}$ denotes from 0 to 2 identical or different substituents from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy and sulfo, preferably from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy and sulfo and especially from the group methyl, methoxy and sulfo,

Y has the definition and preferred meanings given hereinabove, and

Y_1 is a $-CH(Br)-CH_2Br$ or $-C(Br)=CH_2$ group.

In the case of the radicals of formulae (4a') and (4b'), Y is preferably β -chloroethyl. In the case of the radicals of formulae (4c') and (4d'), Y is preferably vinyl or β -sulfoethyl.

A preferred embodiment of the present invention relates to dyes wherein D_1 corresponds to a radical of formula

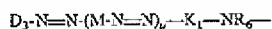


wherein

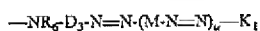
R_5 has the definition and preferred meanings given hereinabove for R_1 , R_{1a} and R_{1b} ,

X_4 has the definition and preferred meanings given hereinabove for X_1 , and is especially chlorine, and

T_3 is a monoazo- or disazo-amino radical of formula



(6) or



(7),

wherein

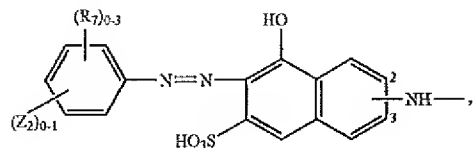
D_3 is the radical of a diazo component, of the benzene or naphthalene series, M is the radical of a middle component, of the benzene or naphthalene series, K_1 is the radical of a coupling component, of the benzene, naphthalene, pyrazolone, 6-hydroxypyridone-(2) or acetoacetic acid arylamide series, R_6 has the definition and preferred meanings given hereinabove for R_1 , R_{1a} and R_{1b} , and u is the number 0 or 1, wherein D_3 , M and K_1 may carry substituents customary for azo dyes.

The expression "substituents customary for azo dyes" is understood to include both fibre-reactive and non-fibre-reactive substituents, such as, for example, the substituents indicated above for D_1 .

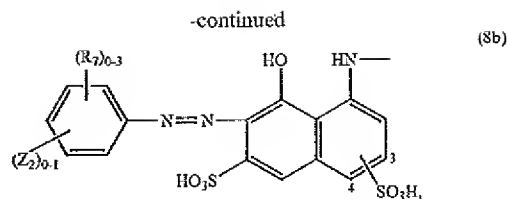
As non-fibre-reactive substituents for D_3 , M and K_1 in T_3 there come into consideration preferably C_1 - C_4 alkyl or C_1 - C_4 alkoxy each of which may themselves be substituted by hydroxy, C_1 - C_4 alkoxy, sulfo or by sulfato; halogen; carboxy; sulfo; nitro; cyano; trifluoromethyl; sulfamoyl; carbamoyl; amino; ureido; hydroxy; sulfomethyl; C_2 - C_4 alkanoylamino; C_1 - C_4 alkylsulfonoylamino; benzoylamino unsubstituted or substituted on the phenyl ring by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen or by sulfo; and phenyl unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy or by sulfo.

The monoazo- or disazo-amino radicals of formula (6) or (7) contain preferably at least one sulfo group.

Preferred monoazo- and disazo-amino radicals T_3 are the radicals of formulae

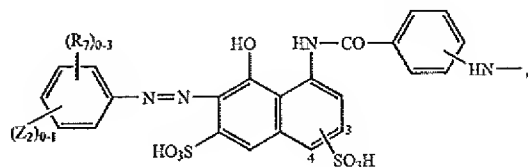


(8a)

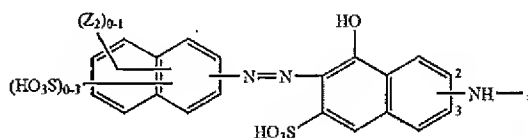


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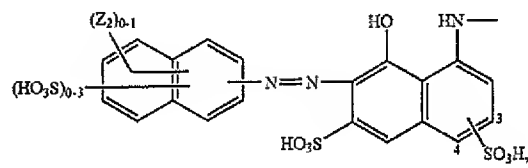
(8b)



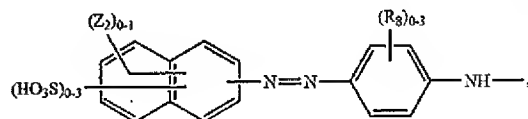
(8c)



(8d)



(8e)

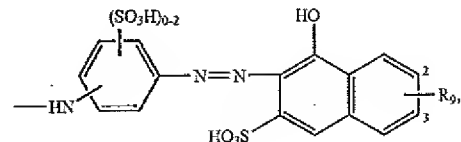


(8f)

wherein $(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, halogen, carboxy and sulfo,

$(R_8)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl; C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy; amino, C_2 - C_4 alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C_1 - C_4 alkylsulfonoylamino and sulfo, preferably from the group halogen, C_1 - C_4 alkyl; C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy; amino, C_1 - C_4 alkanoylamino, ureido and sulfo, and

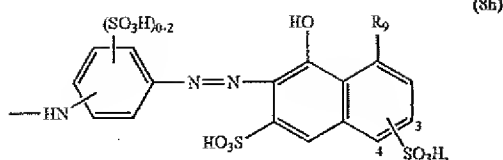
Z_2 is a radical of formula (3a), (3b), (3c), (3d), (3e) or (3f), preferably (3a), (3b), (3c), (3d) or (3e) and especially (3a), the mentioned fibre-reactive radicals having the definitions and preferred meanings given hereinabove,



(8g)

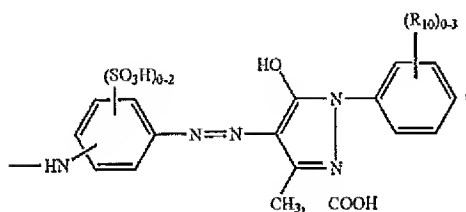
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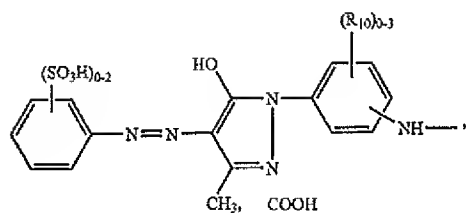


(8b)

wherein R_9 is benzoylamino, C_2 - C_4 alkanoylamino, for example acetyl amino or propionyl amino, or a radical of the above formula (3f), preferably C_2 - C_4 alkanoylamino or benzoylamino, R_{10} , T_1 and X_1 in the radical of formula (3f) each having the definitions and preferred meanings given hereinabove,

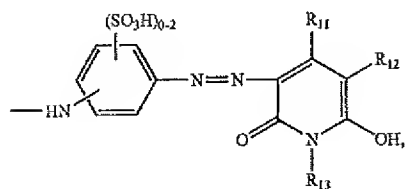


(8i)



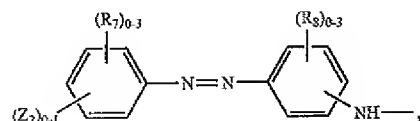
(8j)

wherein $(R_{10})_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy and sulfo,



(8k)

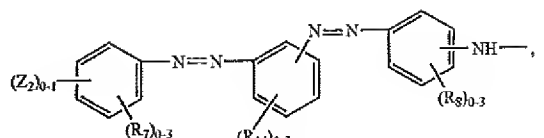
wherein R_{11} and R_{13} are each independently of the other hydrogen, C_1 - C_4 alkyl or phenyl, and R_{12} is hydrogen, cyano, carbamoyl or sulfomethyl,



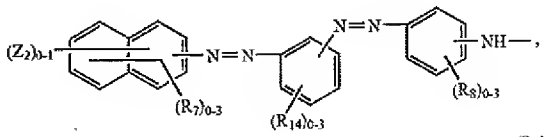
(8l)

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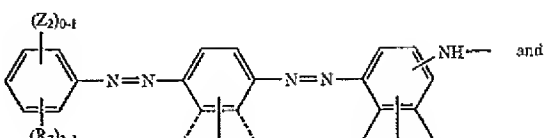
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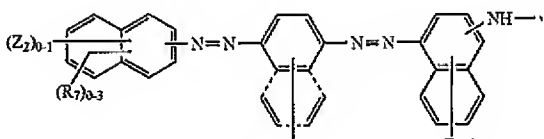
(8m)



(8n)



(8o)



(8p)

wherein

$(R_7)_{0-3}$, $(R_8)_{0-3}$ and $(R_{10})_{0-3}$ each have the definitions and preferred meanings given hereinabove,

$(R_{14})_{0-3}$ and $(R_{15})_{0-3}$ each independently of the other, denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy and sulfo, and Z_2 has the definition and preferred meanings given hereinabove.

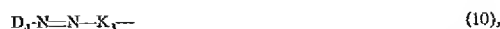
The numbers at the naphthyl rings of the radicals of formulae (8a), (8b), (8c), (8d), (8e), (8g) and (8h) indicate the preferred bonding positions.

The radicals $(R_7)_{0-3}$ in the disazo amino radicals of formulae (8n) and (8p) preferably denote from 0 to 3 sulfo groups.

In an embodiment of interest, Z_2 in the radicals of formulae (8a), (8b), (8c), (8d), (8e), (8f), (8i), (8m), (8n), (8o) and (8p) is hydrogen.

Especially preferred monoazo- and disazo-amino radicals T_3 are the radicals of formulae (8a), (8b), (8d), (8e), (8f), (8k) and (8m), especially (8b), (8e), (8k) and (8m).

In a further preferred embodiment of the present invention, D_1 is a radical of formula



60

preferably of formula (10), wherein D_4 is the radical of a diazo component, of the benzene or naphthalene series, K_2 is the radical of a coupling component, of the benzene, naphthalene, pyrazolone, 6-hydroxypyridone-(2) or acetoacetic acid arylamide series and K_3 is the radical of a coupling component, of the benzene or naphthalene series, wherein D_4 , K_2 and K_3 may carry substituents customary for azo dyes.

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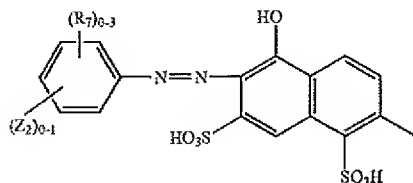
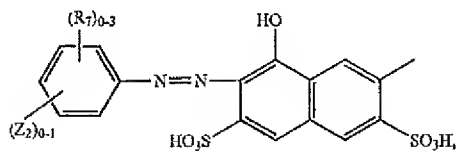
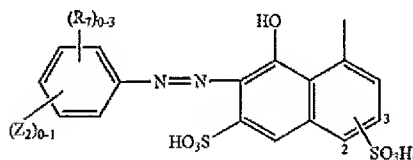
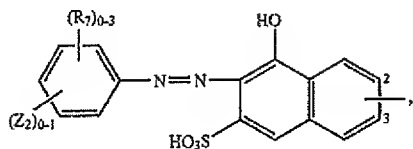
The expression "substituents customary for azo dyes" is understood to include both fibre-reactive and non-fibre-reactive substituents, such as, for example, the substituents indicated above for D_1 .

As non-fibre-reactive substituents for D_4 , K_2 and K_3 there come into consideration preferably C_1 - C_4 alkyl or C_1 - C_4 alkoxy each of which may themselves be substituted by hydroxy, C_1 - C_4 -alkoxy, sulfo or by sulfato; halogen; carboxy; sulfo; nitro; cyano; trifluoromethyl; sulfamoyl; carbamoyl; amino; ureido; hydroxy; sulfomethyl; C_2 - C_4 alkanoylamino; C_1 - C_4 alkylsulfonoylamino; benzoylamino unsubstituted or substituted on the phenyl ring by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen or by sulfo; and phenyl unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy or by sulfo.

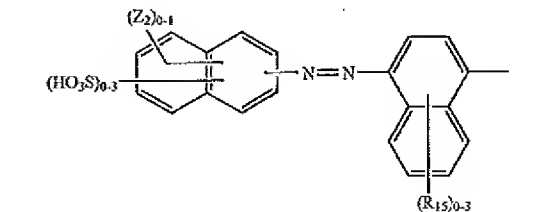
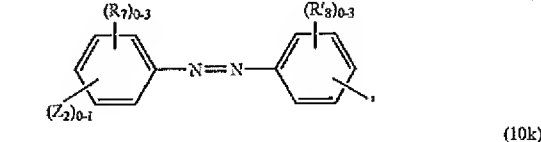
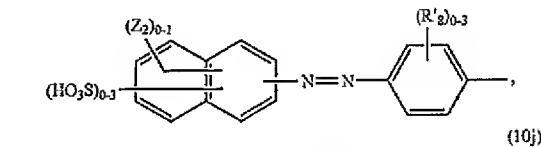
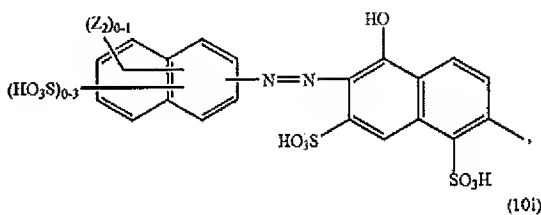
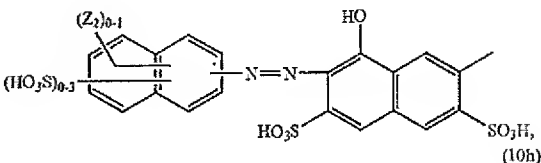
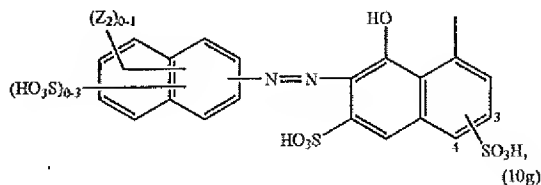
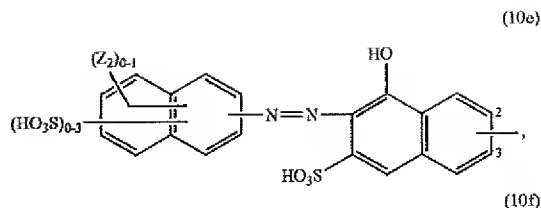
As fibre-reactive substituents for D_4 , K_2 and K_3 there come into consideration preferably the radicals of formulae (3a), (3b), (3c), (3d), (3e) and (3f), especially (3a) and (3f) and more especially (3a), the said radicals having the definitions and preferred meanings given hereinabove. In an embodiment of interest, a radical of formula (3a) is preferred as fibre-reactive substituent for D_4 and a radical of formula (3f) is preferred as fibre-reactive substituent for K_3 .

Monoazo radicals of formula (9) or (10) contain preferably at least one sulfo group.

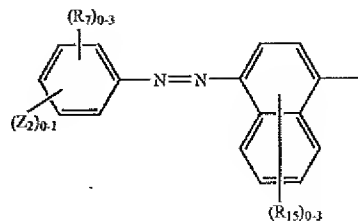
Preferred monoazo radicals D_1 of formula (10) correspond to the radicals of formulae



wherein $(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy and sulfo and Z_2 is a fibre-reactive radical of formula (3a), (3c), (3d), (3e), (3f) or (3g), preferably (3a), (3c), (3d) or (3e) and especially (3a), wherein the said fibre-reactive radicals have the definitions and preferred meanings given hereinabove,



and



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wherein $(R_7)_{0-3}$ is as defined hereinabove, $(R'_3)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl; C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy; amino, C_2 - C_4 alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C_1 - C_4 alkylsulfonfylamino, sulfo and a fibre-reactive radical of formula (3f), preferably from the group C_1 - C_4 alkyl; C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by C_1 - C_4 alkoxy; amino, C_2 - C_4 alkanoylamino, ureido, sulfo and a fibre-reactive radical of formula (3f), wherein R_{1a} , T_1 and X_1 in the radical of formula (3f) have the definitions and preferred meanings given hereinabove, $(R_{15})_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, carboxy and sulfo and is preferably sulfo, and Z_2 has the definition and preferred meanings given hereinabove.

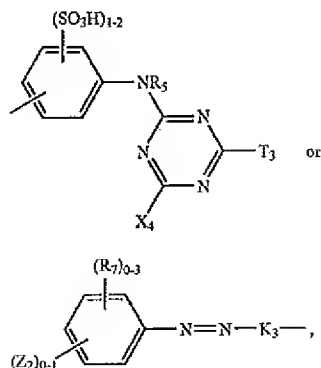
The numbers at the naphthyl rings of the radicals of formulae (10a), (10b), (10e) and (10f) indicate the preferred bonding positions.

When R'_8 is a radical of formula (3f), then especially R_{1a} is hydrogen,

T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring in the same way as phenylamino and in which alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and X_1 is chlorine.

As a radical of formula (10), D_1 is especially preferably a radical of formula (10i), (10j), (10k) or (10l), especially of formula (10j) or (10l).

Preferably, the radical D_1 corresponds to a radical of formula (5) or (11)



wherein

R_5 is hydrogen or C_1 - C_4 alkyl, preferably hydrogen, methyl or ethyl and especially hydrogen,

$(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen,

C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy and sulfo, preferably from the group C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino and sulfo,

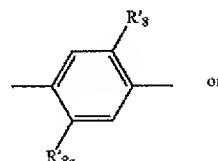
X_4 is fluorine or chlorine, preferably chlorine,

T_3 is a radical of the above formula (8a), (8b), (8d), (8e), (8f), (8k) or (8m), preferably (8b), (8e), (8k) or (8m), wherein the variables have the definitions and preferred meanings given hereinabove,

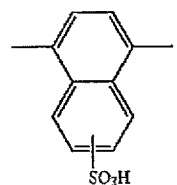
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Z_2 is a fibre-reactive radical of the above formula (3a), (3c), (3d), (3e), (3f) or (3g), preferably (3a), (3c), (3d) or (3e) and especially (3a), wherein the variables have the definitions and preferred meanings given hereinabove, and

K_3 is the radical of a coupling component of formula



(12a)



(12b)

wherein

R'_8 is hydrogen, sulfo, or C_1 - C_4 alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido or a radical of the above formula (3f), preferably hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino or ureido, wherein R_{1a} , T_1 and X_1 in the radical of formula (3f) have the definitions and preferred meanings given hereinabove, and, especially,

R_{1a} is hydrogen,

T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring in the same way as phenylamino and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and X_1 is chlorine.

There come into consideration as C_1 - C_4 alkyl for R_7 and R'_{8a} , each independently of the other, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and isobutyl, preferably methyl and ethyl and especially methyl.

There come into consideration as C_1 - C_4 alkoxy for R_7 , R_8 and R'_{8a} , each independently of the others, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and isobutoxy, preferably methoxy and ethoxy. R_7 and R'_{8a} are especially methoxy. R'_8 is unsubstituted or may be substituted in the alkyl moiety by hydroxy or by sulfato.

There come into consideration as halogen for R_7 , each independently of any other(s), for example, fluorine, chlorine and bromine, preferably chlorine and bromine and especially chlorine.

There come into consideration as C_2 - C_4 alkanoylamino for R_7 and R'_{8a} , for example, acetylamino and propionylamino, especially acetylamino.

There comes into consideration as a radical of formula (3f) for R'_{8a} preferably a radical

wherein

R_{1a} is hydrogen,

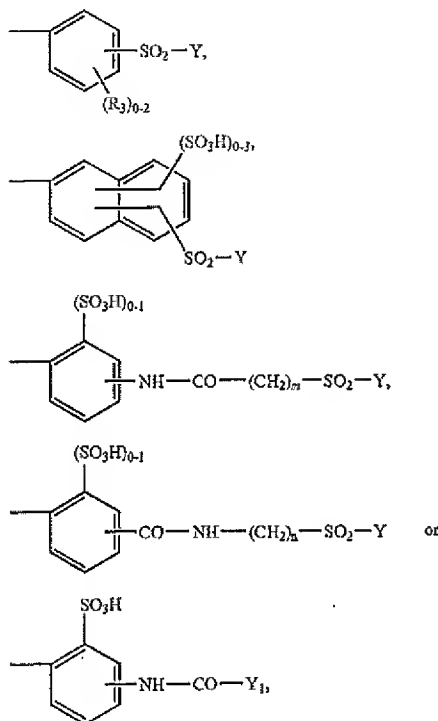
T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino or

N-C₁-C₄alkyl-N-phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetyl amino, chlorine, methyl or by methoxy and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X₁ is fluorine or chlorine, preferably chlorine.

In an embodiment of interest, D₂ corresponds to a radical of formula (2), wherein (Q₃)₀₋₃ and Z₁ each have the definitions and preferred meanings given hereinabove.

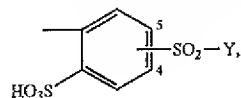
Preferably, the radical D₂ corresponds to a radical of formula



wherein

(R₃)₀₋₂ denotes from 0 to 2 identical or different substituents selected from the group halogen, C₁-C₄alkyl, C₁-C₄alkoxy and sulfo, preferably from the group methyl, methoxy and sulfo, Y₁ is a -CH(Br)-CH₂-Br or -C(Br)=CH₂ group, Y is vinyl or β-sulfatoethyl, m is the number 2 or 3, preferably 2, and n is the number 2 or 3, preferably 3.

Especially preferably, D₂ is a radical of the above formula (2a), (2b) or (2d), especially (2a); in an embodiment of interest the radical of formula (2a) is a radical of formula



wherein

Y is vinyl or β-sulfatoethyl, and

the numbers given in the formula indicate the possible bonding positions of -SO₂-Y, the 4-position being preferred.

A preferred embodiment of the present invention relates to reactive dyes of formula (1)

wherein

Q₁ and Q₂ are hydrogen,

D₁ corresponds to a radical of the above formula (5) or (11) wherein

R₅ is hydrogen or C₁-C₄alkyl, preferably hydrogen, methyl or ethyl and especially hydrogen,

(R₇)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen,

C₁-C₄alkyl, C₁-C₄alkoxy, C₂-C₄alkanoylamino, carboxy and sulfo, preferably from the group C₁-C₄alkyl, C₁-C₄alkoxy, C₂-C₄alkanoylamino and sulfo,

X₄ is fluorine or chlorine, preferably chlorine,

T₃ is a radical of the above formula (8a), (8b), (8d), (8e), (8f), (8k) or (8m), preferably (8b), (8e), (8k) or (8m), wherein the variables have the definitions and preferred meanings given hereinabove,

Z₂ is a fibre-reactive radical of the above formula (3a), (3c), (3d), (3e), (3f) or (3g), preferably (3a), (3c), (3d) or (3e) and especially (3a), wherein the variables have the definitions and preferred meanings given hereinabove, and

K₃ is the radical of a coupling component of the above formula (12a) or (12b) wherein

R₈ is hydrogen, sulfo, or C₁-C₄alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R₁₀ is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, C₂-C₄alkanoylamino, ureido or a radical of the above formula (3f), wherein R₁₀, T₁ and X₁ in the radical of formula (3f) have the definitions and preferred meanings given hereinabove, and

D₂ is a radical of the above formula (2aa) wherein

Y is vinyl or β-sulfatoethyl, and

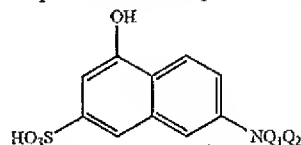
the numbers given in formula (2aa) indicate the possible bonding positions of -SO₂-Y, the 4-position being preferred.

The present invention relates also to a process for the preparation of dyes of formula (1) which comprises

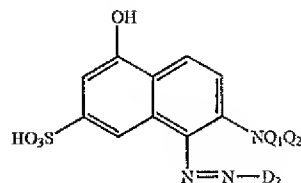
(i) diazotisation of approximately one molar equivalent of an amine of formula



in customary manner and reaction with approximately one molar equivalent of a compound of formula



to form a compound of formula



and

(ii) diazotisation of approximately one molar equivalent of an amine of formula



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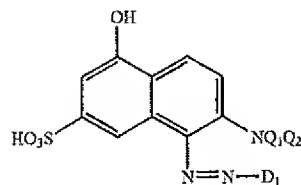
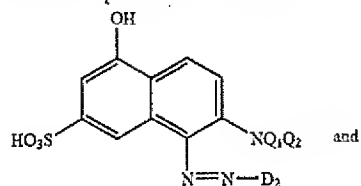
in customary manner and reaction with approximately one molar equivalent of the compound of formula (15a) obtained according to (i) to form a compound of formula (1) wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions and preferred meanings given hereinabove.

The diazotisation of the amines of formulae (13) and (16) is carried out in a manner known per se, for example using a nitrite, for example an alkali metal nitrite such as sodium nitrite, in a mineral acid medium, for example in a hydrochloric acid medium, at temperatures of, for example, from -5 to 40°C . and preferably at from 0 to 20°C .

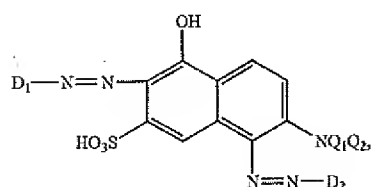
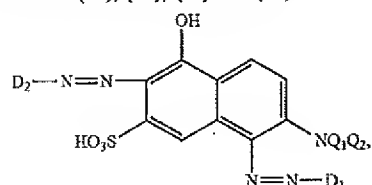
The coupling to the coupling components of formulae (14) and (15a) is carried out in a manner known per se at acidic or neutral to slightly alkaline pH values, for example a pH value of from 0 to 8 , and at temperatures of, for example, from -5 to 40°C ., preferably from 0 to 30°C .

The first coupling—(i)—takes place in an acidic medium, for example at a pH of from 0 to 4 , and the second coupling—(ii)—at elevated pH values, in a slightly acidic, neutral or slightly alkaline medium, for example a pH value of from 4 to 8 .

By proceeding as described hereinabove but, instead of using approximately one molar equivalent each of the amines of formulae (13) and (16) in process steps (i) and (ii), using in each case approximately one molar equivalent of a mixture of at least two, preferably two, non-identical amines, for example a 1:1 molar mixture of the compounds of formulae (13) and (16), there is obtained first of all, according to (i), a mixture of compounds of formulae

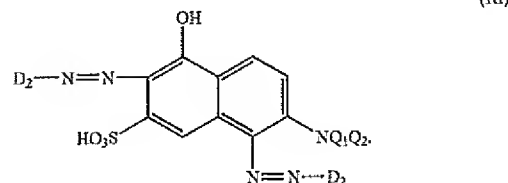
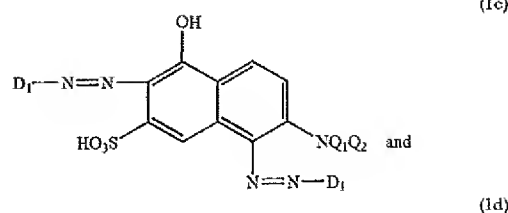


and, on further reaction of the mixture of compounds of formulae (15a) and (15b) according to (ii), a mixture of dyes of formulae (1a), (1b), (1c) and (1d)



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-continued



The present invention accordingly relates also to dye mixtures that comprise at least one dye of formulae (1a) and (1b) together with at least one dye of formulae (1c) and (1d), especially one dye each of formulae (1a), (1b), (1c) and (1d), wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions and preferred meanings given hereinabove and D_1 and D_2 are not identical.

The ratio of the dyes of formulae (1a), (1b), (1c) and (1d) in the mixture can vary within wide limits and depends on the ratio of the particular amines $D_1\text{-NH}_2$ and $D_2\text{-NH}_2$ used according to (i) and (ii).

The above dye mixtures contain, for example, from 5 to 95% by weight, especially from 10 to 90% by weight and preferably from 20 to 80% by weight, of a dye of formula (1a) and/or (1b), based on the total amount of the dyes of formulae (1a), (1b), (1c) and (1d) in the mixture.

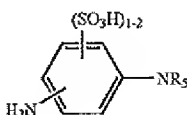
Where appropriate, the end product may, in addition, be subjected to a conversion reaction. Such a conversion reaction is, for example, the conversion of the radical Y denoting $\text{—CH}_2\text{CH}_2\text{—U}$ or another reactive group capable of conversion to a vinyl moiety into the corresponding vinyl form by treatment with dilute sodium hydroxide solution, such as, for example, the conversion of the β -sulfoethylsulfonyl or β -chloroethylsulfonyl group into the vinylsulfonyl radical. Such reactions are known per se.

The compounds of formulae (13), (14) and (16) are known or can be obtained in a manner known per se.

For example, the compound of formula (16) wherein D_1 is a radical of the above formula (5) can be prepared by condensation of approximately one molar equivalent of 2,4,6-trichloro-s-triazine or 2,4,6-trifluoro-s-triazine first with approximately one molar equivalent of a compound of formula



at a pH value in the neutral range and at low temperature, for example from 0 to 5°C ., and then with approximately one molar equivalent of a compound of formula



at a slightly acidic to neutral pH value, for example pH 4.5-7.5, and at a temperature of, for example, from 0 to 30° C.

Such condensation reactions are known and are described, for example, in EP-A-0 260 227 and U.S. Pat. No. 4,841,049.

Instead of the compound of formula (17), a preliminary product, for example a diazo component or coupling component, may alternatively be used in the process, the radical T₃ being produced only in the further course of the process by a corresponding diazotisation and coupling reaction.

The reactive dyes according to the invention are either in the form of their free acids or, preferably, in the form of salts thereof. Salts that come into consideration are, for example, alkali metal, alkaline earth metal and ammonium salts, and salts of an organic amine. Sodium, lithium, potassium and ammonium salts and the salt of the mono-, di- or tri-ethanolamine may be mentioned as examples.

The reactive dyes according to the invention are suitable for dyeing and printing an extremely wide variety of materials, especially hydroxyl-group-containing or nitrogen-containing fibre materials. Examples are paper, silk, leather, wool, polyamide fibres and polyurethanes and also especially cellulosic fibre materials of all kinds. Such fibre materials are, for example, natural cellulosic fibres, such as cotton, linen and hemp, and also cellulose and regenerated cellulose. The dyes according to the invention are also suitable for dyeing or printing hydroxyl-group-containing fibres present in blend fabrics, e.g. blends of cotton with polyester fibres or polyamide fibres.

The present invention accordingly relates also to the use of the reactive dyes according to the invention in the dyeing or printing of hydroxyl-group-containing or nitrogen-containing, especially cotton-containing, fibre materials.

The reactive dyes according to the invention can be applied to the fibre material and fixed to the fibre in a variety of ways, especially in the form of aqueous dye solutions and dye print pastes. They are suitable both for the exhaust method and for dyeing in accordance with the pad-dyeing method; they can be used at low dyeing temperatures and require only short steaming times in the pad-steam process. The degrees of fixing are high and unfixed dye can be washed off easily, the difference between the degree of exhaust and the degree of fixing being remarkably small, that is to say the soaping loss being very low. The reactive dyes according to the invention are also suitable for printing, especially on cotton, but are equally suitable also for printing nitrogen-containing fibres, for example wool or silk or blend fabrics that contain wool.

The dyeings and prints produced using the reactive dyes according to the invention have a high tinctorial strength and a high fibre-to-dye binding stability in both the acidic and the alkaline range, and furthermore have good fastness to light and very good wet-fastness properties, such as fastness to washing, to water, to sea water, to cross-dyeing and to perspiration. The dyeings obtained exhibit fibre levelness and surface levelness.

The present invention relates furthermore to aqueous inks that comprise a reactive dye of formula (1) wherein Q₁, Q₂, D₁ and D₂ each have the definitions and preferred meanings given hereinabove.

The dyes used in the inks should preferably have a low salt content, that is to say they should have a total content of salts of less than 0.5% by weight, based on the weight of the dyes. Dyes that have relatively high salt contents as a result of their preparation and/or as a result of the subsequent addition of diluents can be desalted, for example, by membrane separation procedures, such as ultrafiltration, reverse osmosis or dialysis.

The inks preferably have a total content of dyes of from 1 to 35% by weight, especially from 1 to 30% by weight and preferably from 1 to 20% by weight, based on the total weight of the ink. The preferred lower limit in this case is a limit of 1.5% by weight, preferably 2% by weight and especially 3% by weight.

The inks may comprise water-miscible organic solvents, for example C₁-C₄ alcohols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol or iso-butanol; amides, e.g. dimethylformamide or dimethylacetamide; ketones or ketone alcohols, e.g. acetone, diacetone alcohol; ethers, e.g. tetrahydrofuran or dioxane; nitrogen-containing heterocyclic compounds, e.g. N-methyl-2-pyrrolidone or 1,3-dimethyl-2-imidazolidone, poly-alkylene glycols, e.g. polyethylene glycol or polypropylene glycol; C₂-C₆ alkylene glycols and thioglycols, e.g. ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, thiodiglycol, hexylene glycol and dichylene glycol; other polyols, e.g. glycerol or 1,2,6-hexane-triol; and C₁-C₄ alkyl ethers of polyhydric alcohols, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol or 2-[2-(2-ethoxyethoxy)ethoxy]ethanol; preferably N-methyl-2-pyrrolidone, diethylene glycol, glycerol or especially 1,2-propylene glycol, usually in an amount of from 2 to 30% by weight, especially from 5 to 30% by weight and preferably from 10 to 25% by weight, based on the total weight of the ink.

In addition, the inks may also comprise solubilisers, e.g. ϵ -caprolactam.

The inks may comprise thickeners of natural or synthetic origin inter alia for the purpose of adjusting the viscosity.

Examples of thickeners that may be mentioned include commercially available alginate thickeners, starch ethers or locust bean flour ethers, especially sodium alginate on its own or in admixture with modified cellulose, e.g. methyl cellulose, ethyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, methyl hydroxyethyl cellulose, hydroxypropyl cellulose or hydroxypropyl methyl cellulose, especially with preferably from 20 to 25% by weight carboxymethyl cellulose. Synthetic thickeners that may be mentioned are, for example, those based on poly(meth)acrylic acids or poly(meth)acrylamides.

The inks comprise such thickeners, for example, in an amount of from 0.01 to 2% by weight, especially from 0.01 to 1% by weight and preferably from 0.01 to 0.5% by weight, based on the total weight of the ink.

The inks may also comprise buffer substances, e.g. borax, borates, phosphates, polyphosphates or citrates. Examples that may be mentioned include borax, sodium borate, sodium tetraborate, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium triphosphate, sodium pentaphosphate and sodium citrate. They are used especially in amounts of from 0.1 to 3% by weight, preferably from 0.1 to 1% by weight, based on the total weight of the ink, in order to establish a pH value of, for example, from 4 to 9, especially from 5 to 8.5.

As further additives, the inks may comprise surfactants or humectants.

Suitable surfactants include commercially available anionic or non-ionic surfactants. As humectants in the inks according to the invention there come into consideration, for example, urea or a mixture of sodium lactate (advantageously in the form of a 50% to 60% aqueous solution) and glycerol and/or propylene glycol in amounts of preferably from 0.1 to 30% by weight, especially from 2 to 30% by weight.

Preference is given to inks having a viscosity of from 1 to 40 mPa·s, especially from 1 to 20 mPa·s and more especially from 1 to 10 mPa·s.

Furthermore, the inks may in addition comprise customary additives, e.g. anti-foams or especially substances that inhibit fungal and/or bacterial growth. Such additives are usually used in amounts of from 0.01 to 1% by weight, based on the total weight of the ink.

The inks can be prepared in customary manner by mixing together the individual constituents in the desired amount of water.

The inks according to the invention are suitable especially for use in recording systems of a kind in which an ink is forced out of a small aperture in the form of droplets that are directed onto a substrate on which an image is formed. Suitable substrates are, for example, paper, textile fibre materials or plastics films. Suitable recording systems are, for example commercially available inkjet printers for use in paper or textile printing, or writing instruments, such as fountain pens or ballpoint pens, and especially inkjet printers.

Depending on the use, it may be necessary, for example, for the viscosity or other physical properties of the ink, especially properties that have an influence on the affinity for the substrate in question, to be adapted accordingly.

As examples of paper that can be printed with the inks according to the invention there may be mentioned commercially available ink-jet paper, photo paper, glossy paper, plastics-coated paper, e.g. Epson Ink-jet Paper, Epson Photo Paper, Epson Glossy Paper, Epson Glossy Film, HP Special Ink-jet Paper, Encad Photo Gloss Paper and Ilford Photo Paper. Plastics films that can be printed with the inks according to the invention are, for example, transparent or cloudy/opaque. Suitable plastics films are, for example, 3M Transparency Film.

As textile fibre materials there come into consideration, for example, nitrogen-containing or hydroxy-group-containing fibre materials, for example textile fibre materials of cellulose, silk, wool or synthetic polyamides, preferably cellulose.

The present invention accordingly relates also to a method of printing textile fibre materials, paper or plastics films, preferably textile fibre materials or paper, and especially textile fibre materials, according to the ink-jet printing method, which comprises using an aqueous ink that comprises a reactive dye of formula (1) wherein Q_1 , Q_2 , D_1 and D_2 each have the definitions and preferred meanings given hereinabove.

In the case of the ink-jet printing method, individual droplets of ink are sprayed onto a substrate from a nozzle in a controlled manner. It is mainly the continuous ink-jet method

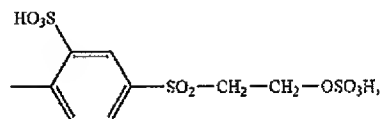
and the drop-on-demand method that are used for that purpose. In the case of the continuous ink-jet method, the droplets are produced continuously, droplets not required for the printing operation being discharged into a receptacle and recycled. In the case of the drop-on-demand method, on the other hand, droplets are generated as desired and used for printing; that is to say, droplets are generated only when required for the printing operation. The production of the droplets can be effected, for example, by means of a piezo ink-jet head or by thermal energy (bubble jet). For the process according to the invention, printing by means of a piezo ink-jet head is preferred, but preference is given also to printing according to the continuous ink-jet method.

The recordings, for example prints, produced are distinguished especially by a high tinctorial strength and a high colour brilliancy as well as by good light-fastness and wet-fastness properties.

The following Examples serve to illustrate the invention. Unless otherwise indicated, the temperatures are given in degrees Celsius, parts are parts by weight and percentages relate to % by weight. Parts by weight relate to parts by volume in a ratio of kilograms to litres.

EXAMPLE 1

32.5 parts of an amine of formula $D_{10}-NH_2$, wherein D_{10} is a radical of formula



are introduced into 100 parts of water and stirred well. At 10° C., there are added to the resulting suspension first of all 22.8 parts of a 4N sodium nitrite solution and then 41 parts of a 31% naphthalenesulfonic acid solution. Stirring is then carried out for 3 hours at from 15 to 20° C.

EXAMPLES 2 to 19

The diazo compounds of the amines indicated in Table 1 can be prepared analogously to the procedure described in Example 1 by using, instead of the amine of formula $D_{10}-NH_2$ mentioned in Example 1, an equimolar amount of the amines of formula $D_{xy}-NH_2$ indicated in Table 1.

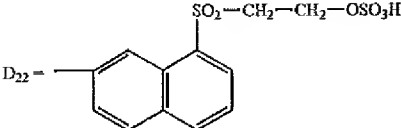
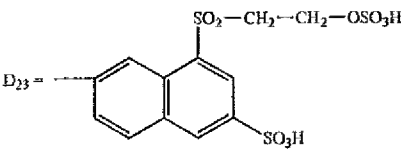
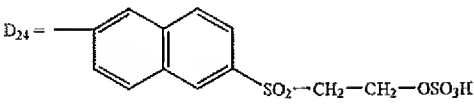
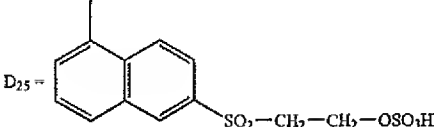
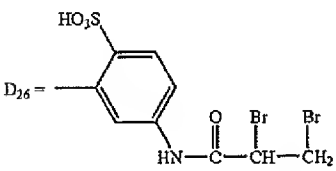
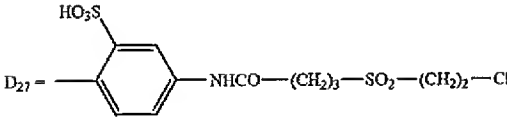
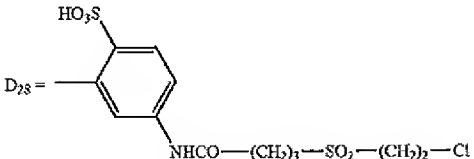
TABLE 1

Ex.	Amine $D_{xy}-NH_2$	D_{xy}
2	$D_{11}-NH_2$	
3	$D_{12}-NH_2$	

TABLE 1-continued

Ex.	Amine D _{xy} -NH ₂	D _{xy}
4	D ₁₃ -NH ₂	
5	D ₁₄ -NH ₂	
6	D ₁₅ -NH ₂	
7	D ₁₆ -NH ₂	
8	D ₁₇ -NH ₂	
9	D ₁₈ -NH ₂	
10	D ₁₉ -NH ₂	
11	D ₂₀ -NH ₂	
12	D ₂₁ -NH ₂	

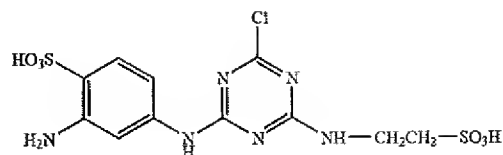
TABLE 1-continued

Ex.	Amine $D_{xy}-NH_2$	D_{xy}
13	$D_{22}-NH_2$	
14	$D_{23}-NH_2$	
15	$D_{24}-NH_2$	
16	$D_{25}-NH_2$	
17	$D_{26}-NH_2$	
18	$D_{27}-NH_2$	
19	$D_{28}-NH_2$	

50

EXAMPLE 20

a) 36.9 parts of cyanuric chloride are stirred in 150 parts of ice/water and a small amount of wetting agent. At from 0 to 2° C., a solution of 25.25 parts of taurine in 50 parts of water is introduced in the course of 40 minutes and condensation is carried out at a pH of from 7 to 8 by the dropwise addition of 2N sodium hydroxide solution. Stirring is then carried out at from 0 to 5° C. and a pH of from 7 to 7.5 until cyanuric chloride can no longer be detected. A neutral solution of 39.48 parts of 1,3-phenylenediamine-4-sulfonic acid in 100 parts of water is then added. Condensation is carried out at a temperature of from 5 to 20° C. and the pH is maintained at from 8 to 9 by the addition of 2N sodium hydroxide solution. When condensation is complete, the reaction solution is salted out using KCl, filtered and washed with concentrated KCl solution. After drying, the intermediate of formula

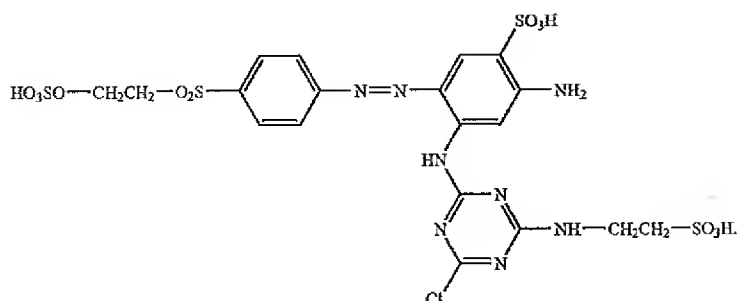


is obtained.

b) 68 parts of the compound according to a) are suspended in 300 parts of water. The diazotized amine from Example 3, which is prepared according to Example 1 from 45 parts of the amine of formula $D_{12}-NH_2$, is then added in the course of 10 minutes at from 0 to 5° C., and the pH is maintained at from 6 to 8.5 using soda solution (20%). When coupling is complete, the yellow dye is precipitated using KCl, and the sus-

27

pension obtained is filtered and dried in vacuo, yielding the monoazo compound of formula



28

(λ_{max} : 550 nm), which dyes wool and cellulose in a bluish violet shade having good allround fastness properties.

(101)

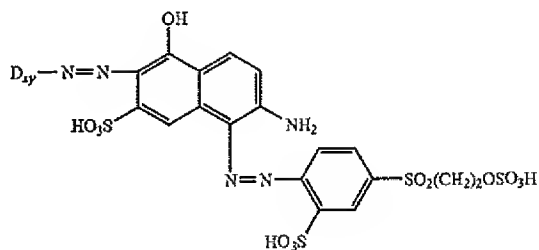
c) 83 parts of the compound according to Example b) are dissolved in 700 parts of water and diazotized according to the customary method with sodium nitrite and HCl at from 0 to 5° C.

EXAMPLE 21

A solution of 21.5 parts of 2-amino-5-naphthol-7-sulfonic acid in 250 parts of water (pH 7) is added dropwise at from 0 to 5° C. to the acid suspension of the diazo compound of the amine of formula D_{10} -NH₂ obtained according to Example 1. The mixture is then heated to room temperature and stirred for approximately 5 h until coupling is complete (first coupling). The reaction mixture is then cooled to from 5 to 10° C., the pH value is increased to approximately 4.5 using an aqueous sodium hydrogen carbonate solution, and the suspension of the diazo compound obtained according to Example 20c) is slowly added dropwise, the pH value being maintained during the dropwise addition at approximately 4.5 by the addition of an aqueous sodium hydrogen carbonate solution and the temperature being maintained at approximately 5° C. After the dropwise addition, the pH value is adjusted to 6 (second coupling). When coupling is complete, the dye solution is freed of salt by dialysis and concentrated by evaporation in vacuo. A compound is obtained which in the form of the free acid corresponds to formula

EXAMPLES 22 TO 39v

A compound of the general formula



can be prepared analogously to the procedure described in Example 21 by using, instead of the amine of formula (101), an equimolar amount of one of the amines of formula D_{xy} -NH₂ indicated in Table 2. The dyes dye wool and cellulose in orange to blue shades having good allround fastness properties.

(102)

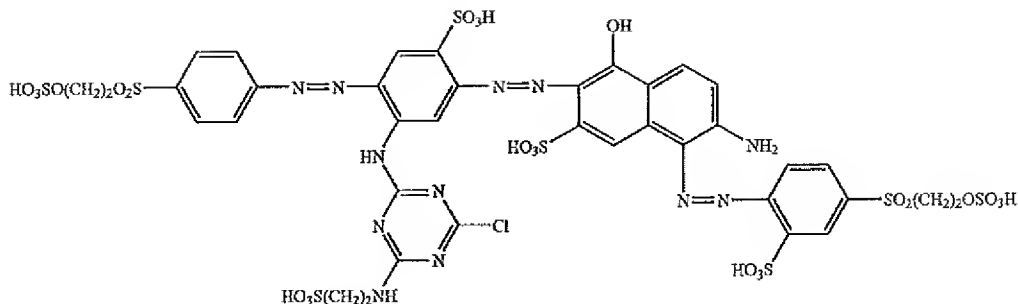


TABLE 2

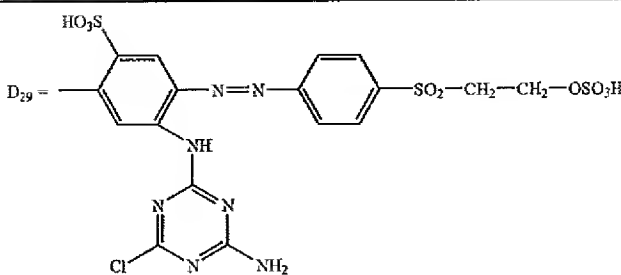
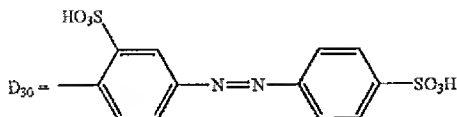
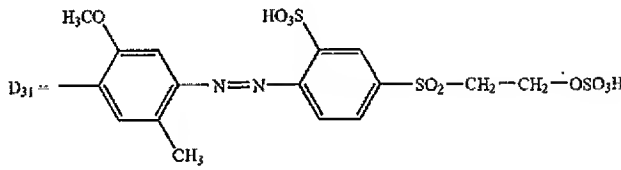
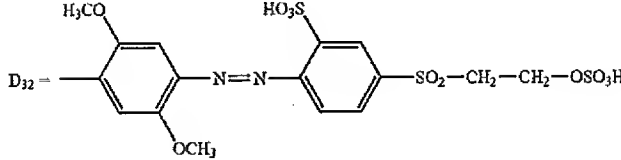
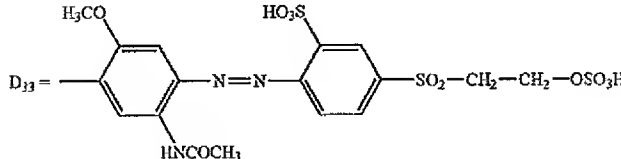
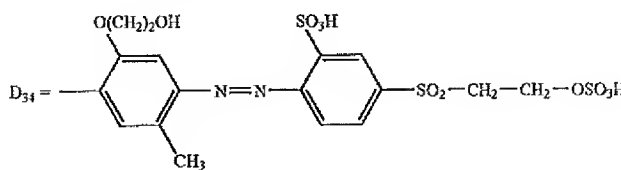
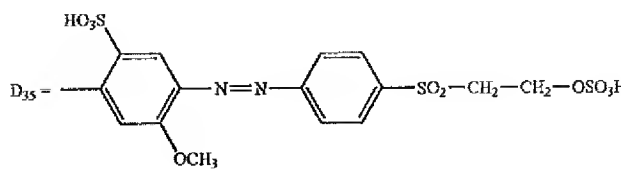
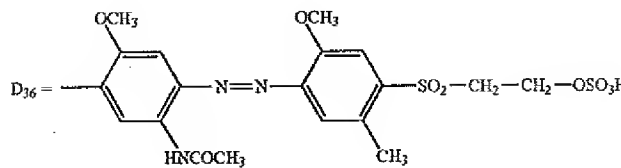
Ex.	Amine $D_{xy}-NH_2$	D_{xy}	λ_{max} [nm]
22	$D_{29}-NH_2$	 <p>$D_{29} =$ <chem>OS(=O)c1ccc(cc1)/N=N/c2ccc(cc2)S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	550
23	$D_{30}-NH_2$	 <p>$D_{30} =$ <chem>OS(=O)c1ccc(cc1)/N=N/c2ccc(cc2)S(=O)(=O)O</chem></p>	536
24	$D_{31}-NH_2$	 <p>$D_{31} =$ <chem>COc1cc(C)ccc1/N=N/c2ccc(cc2)S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	570
25	$D_{32}-NH_2$	 <p>$D_{32} =$ <chem>COc1cc(OC)ccc1/N=N/c2ccc(cc2)S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	583
26	$D_{33}-NH_2$	 <p>$D_{33} =$ <chem>COc1cc(NC(=O)C)ccc1/N=N/c2ccc(cc2)S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	572
27	$D_{34}-NH_2$	 <p>$D_{34} =$ <chem>OC(CO)c1cc(C)ccc1/N=N/c2ccc(cc2)S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	570
28	$D_{35}-NH_2$	 <p>$D_{35} =$ <chem>OS(=O)c1ccc(cc1)Oc2ccccc2S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	536
29	$D_{36}-NH_2$	 <p>$D_{36} =$ <chem>COc1cc(NC(=O)C)ccc1/N=N/c2cc(OC)c(C)ccc2S(=O)(=O)OCCOS(=O)(=O)O</chem></p>	570

TABLE 2-continued

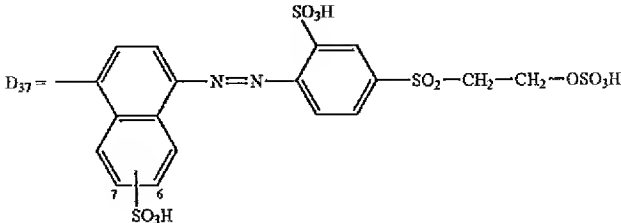
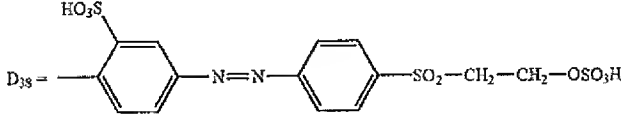
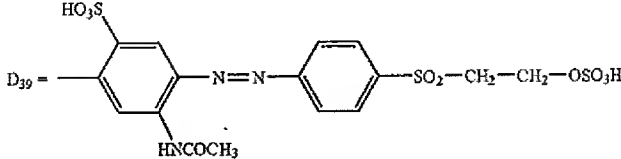
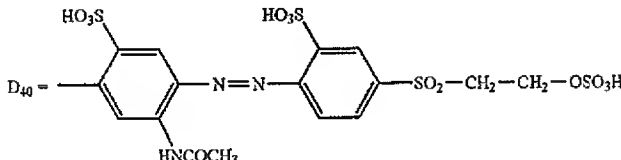
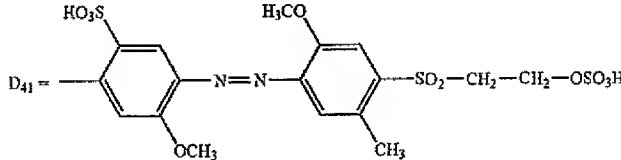
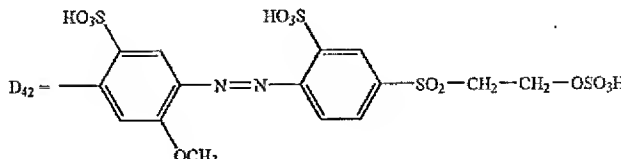
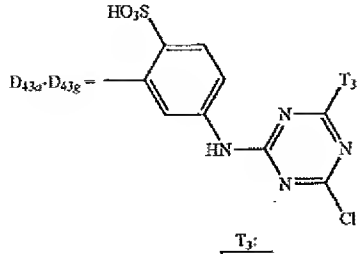
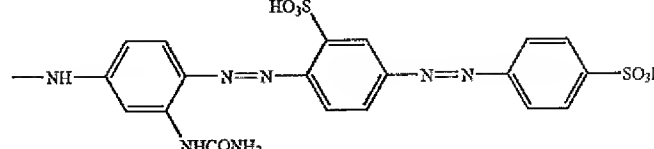
30	D ₃₇ -NH ₂		574
31	D ₃₈ -NH ₂		535
32	D ₃₉ -NH ₂		541
33	D ₄₀ -NH ₂		540
34	D ₄₁ -NH ₂		543
35	D ₄₂ -NH ₂		538
36	D _{43a} -NH ₂ - D _{43b} -NH ₂		
36a	D _{43a} -NH ₂		501

TABLE 2-continued

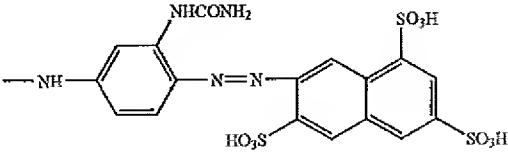
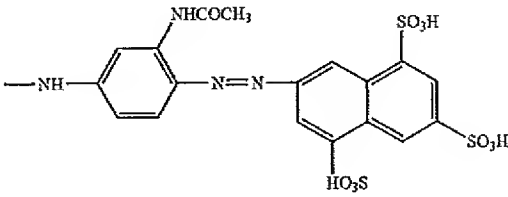
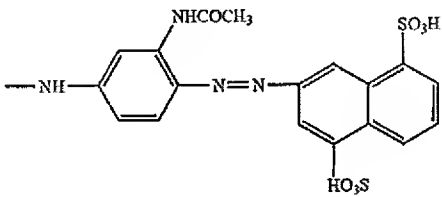
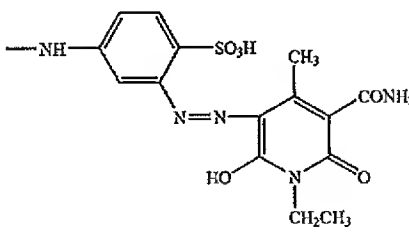
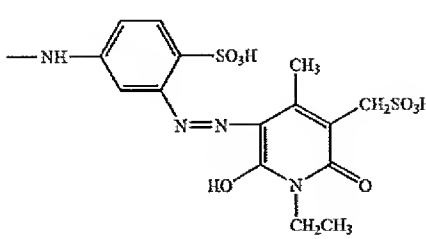
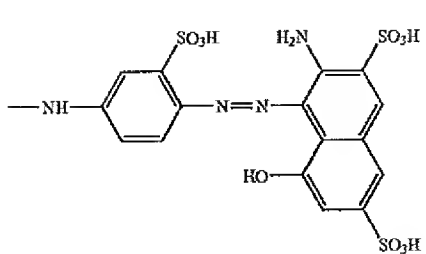
36b	D _{43b} -NH ₂	D _{41b}		488
36c	D _{43c} -NH ₂	D _{41c}		486
36d	D _{43d} -NH ₂	D _{41d}		505
36e	D _{43e} -NH ₂	D _{41e}		516
36f	D _{43f} -NH ₂	D _{41f}		520
36g	D _{43g} -NH ₂	D _{41g}		520

TABLE 2-continued

37	$D_{44a}-NH_2 - D_{44g}-NH_2$			
37a	$D_{44a}-NH_2$	D_{44a}		495
37b	$D_{44b}-NH_2$	D_{44b}		489
37c	$D_{44c}-NH_2$	D_{44c}		487
37d	$D_{44d}-NH_2$	D_{44d}		497
37e	$D_{44e}-NH_2$	D_{44e}		514
37f	$D_{44f}-NH_2$	D_{44f}		513

TABLE 2-continued

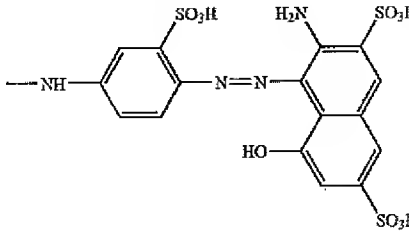
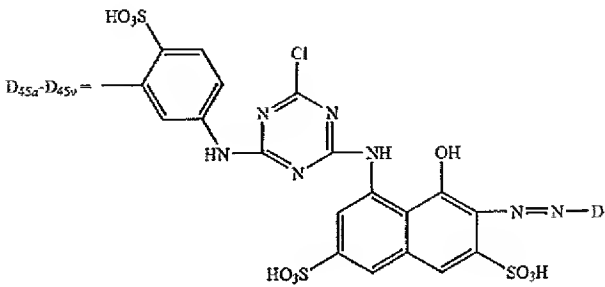
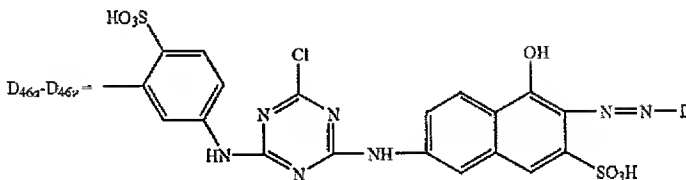
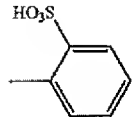
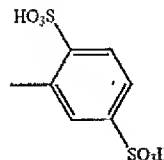
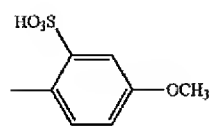
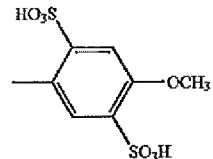
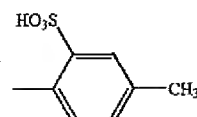
37g	D _{44g} -NH ₂	D _{44g}		514
38	D _{45a} -NH ₂ - D _{45v} -NH ₂	D _{45a} -D _{45v}		
39	D _{46a} -NH ₂ - D _{46v} -NH ₂	D _{46a} -D _{46v}		
			D:	
38a/39a	D _{45a/46a} -NH ₂	D _{45a/46a}		516 (39a) 497 (40a)
38b/39b	D _{45b/46b} -NH ₂	D _{45b/46b}		493 (40b)
38c/39c	D _{45c/46c} -NH ₂	D _{45c/46c}		503 (40c)
38d/39d	D _{45d/46d} -NH ₂	D _{45d/46d}		518 (39d)
38e/39e	D _{45e/46e} -NH ₂	D _{45e/46e}		510 (39e)

TABLE 2-continued

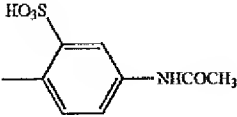
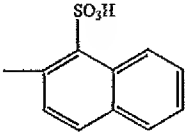
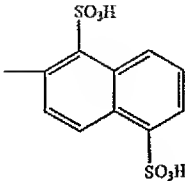
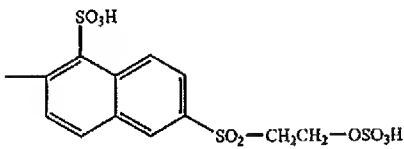
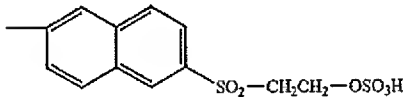
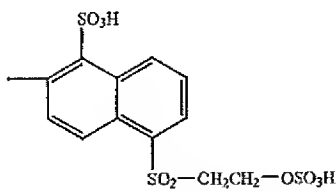
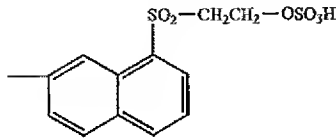
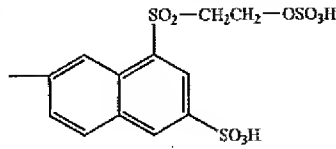
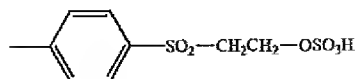
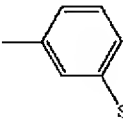
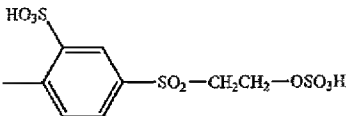
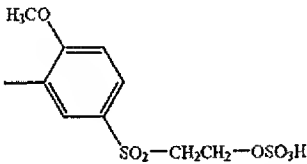
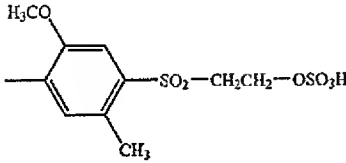
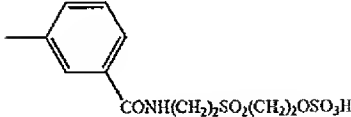

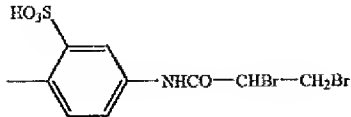
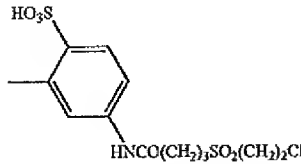
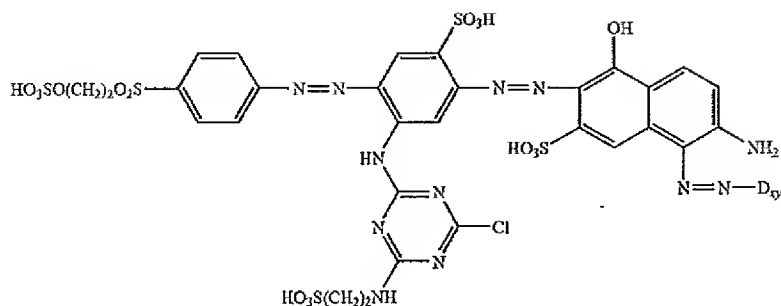
38f/39f	D _{45f/46f} -NH ₂	D _{45f/46f}		524 (39f)
38g/39g	D _{45g/46g} -NH ₂	D _{45g/46g}		520 (39g)
38h/39h	D _{45h/46h} -NH ₂	D _{45h/46h}		518 (39h)
38i/39i	D _{45i/46i} -NH ₂	D _{45i/46i}		520 (39i)
38j/39j	D _{45j/46j} -NH ₂	D _{45j/46j}		528 (39j)
38k/39k	D _{45k/46k} -NH ₂	D _{45k/46k}		518 (39k)
38l/39l	D _{45l/46l} -NH ₂	D _{45l/46l}		522 (39l)
38m/39m	D _{45m/46m} -NH ₂	D _{45m/46m}		520 (39m)
38n/39n	D _{45n/46n} -NH ₂	D _{45n/46n}		510 (39n)

TABLE 2-continued

38o/39o	D _{45o/46o} -NH ₂	D _{45o/46o}		508 (39o)
38p/39p	D _{45p/46p} -NH ₂	D _{45p/46p}		512 (39p)
38q/39q	D _{45q/46q} -NH ₂	D _{45q/46q}		525 (39q)
38r/39r	D _{45r/46r} -NH ₂	D _{45r/46r}		520 (39r)
38s/39s	D _{45s/46s} -NH ₂	D _{45s/46s}		519 (39s)
38t/39t	D _{45t/46t} -NH ₂	D _{45t/46t}		508 (39t)
38u/39u	D _{45u/46u} -NH ₂	D _{45u/46u}		525 (39u)
38v/39v	D _{45v/46v} -NH ₂	D _{45v/46v}		514 (39v)

By proceeding as described in Example 21 but, instead of using the acid suspension of the diazo compound of the amine of formula $D_{10}-NH_2$, using an equimolar amount of the diazo compound of an amine of formula $D_{xy}-NH_2$, a dye of formula



is obtained wherein D_{xy} corresponds to one of the radicals listed in Table 3, the definitions given in Table 1 applying to that radical. The dyes dye wool and cellulose in bluish violet shades having good allround fastness properties.

TABLE 3

Ex.	D_{xy}	
40	D_{11}	
41	D_{12}	40
42	D_{13}	
43	D_{14}	
44	D_{15}	
45	D_{16}	45
46	D_{17}	
47	D_{18}	
48	D_{19}	
49	D_{20}	
50	D_{21}	50
51	D_{22}	
52	D_{23}	
53	D_{24}	
54	D_{25}	55
55	D_{26}	
56	D_{27}	
57	D_{28}	

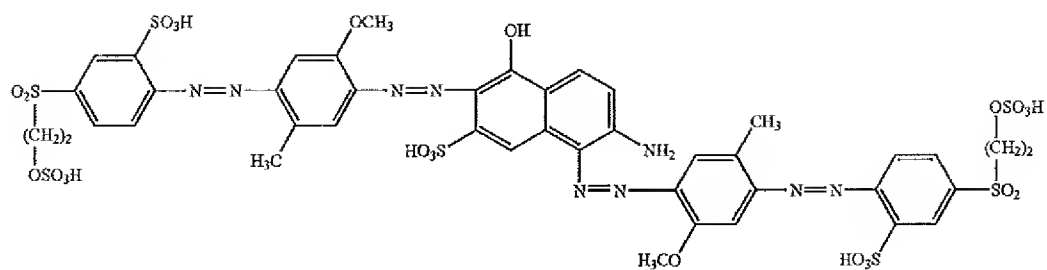
EXAMPLES 58 TO 62

The compounds of the following formulae can be prepared analogously to the procedure described in Example 21

45

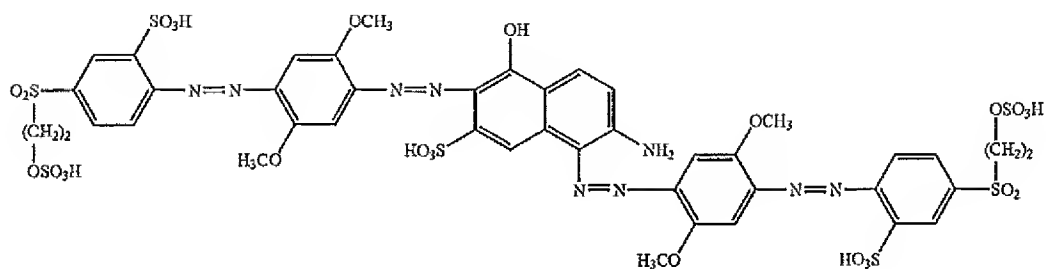
46

(103)

 $(\lambda_{\text{max}}: 588 \text{ nm})$

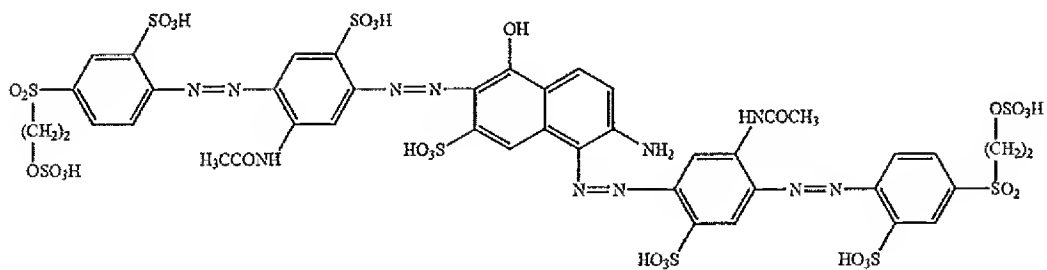
58

(104)

 $(\lambda_{\text{max}}: 604 \text{ nm})$

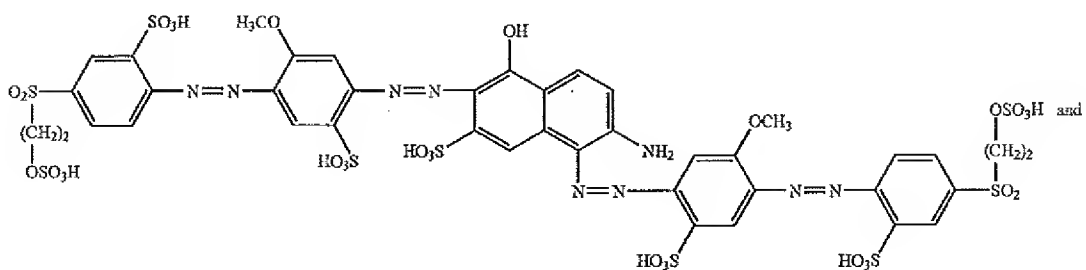
59

(105)

 $(\lambda_{\text{max}}: 554 \text{ nm})$

60

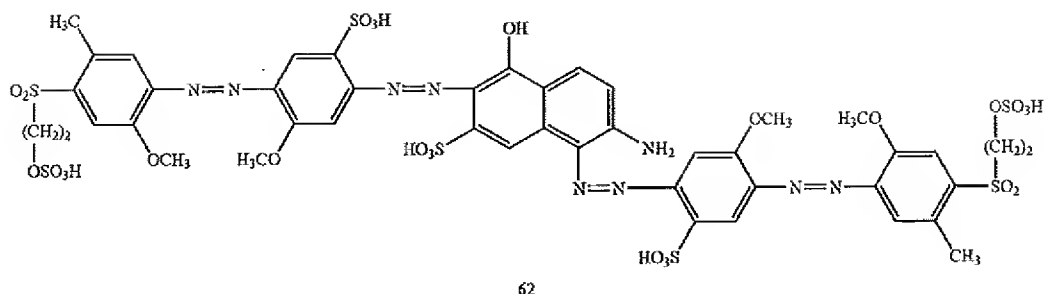
(106)

 $(\lambda_{\text{max}}: 555 \text{ nm})$

61

-continued

(107)



62

which dye wool and cellulose in violet to dark-blue shades having good allround fastness properties.

Dyeing Procedure I

100 parts of cotton fabric are introduced at 60° C. into 1500 parts of a dye bath containing 45 g/l of sodium chloride and 2 parts of the reactive dye obtained according to Example 21. After 45 minutes at 60° C., 20 g/l of calcined soda are added. Dyeing is continued for a further 45 minutes at that temperature. The dyed goods are then rinsed, soaped at the boil for a quarter of an hour with a non-ionic detergent, rinsed again and dried.

As an alternative to the above procedure, the dyeing can be carried out at 80° C. instead of at 60° C.

Dyeing Procedure II

0.1 part of the dye according to Example 21 is dissolved in 200 parts of water, and 0.5 part of sodium sulfate, 0.1 part of a levelling agent (based on the condensation product of a higher aliphatic amine and ethylene oxide) and also 0.5 part of sodium acetate are added. The pH is then adjusted to a value of 5.5 using acetic acid (80%). The dye bath is heated at 50° C. for 10 minutes and then 10 parts of a woollen fabric are added. Heating is then carried out in the course of approximately 50 minutes to a temperature of 100° C. and dyeing is carried out at that temperature for 60 minutes, after which the dye bath is allowed to cool and the dyed goods are removed. The woollen fabric is washed with hot and cold water, and is then spun and dried.

Printing Procedure I

3 parts of the dye obtained according to Example 21 are sprinkled, with rapid stirring, into 100 parts of a stock thickener containing 50 parts of 5% sodium alginate thickener, 27.8 parts of water, 20 parts of urea, 1 part of sodium m-nitrobenzenesulfonate and 1.2 parts of sodium hydrogen carbonate. The print paste so obtained is used to print a cotton fabric, and the resulting printed material is dried and steamed in saturated steam for 2 minutes at 102° C. The printed fabric is then rinsed, if desired soaped at the boil and rinsed again, and subsequently dried.

Printing Procedure II

(a) Mercerised cotton satin is pad-dyed with a liquor containing 30 g/l of sodium carbonate and 50 g/l of urea (70% liquor pick-up) and dried.

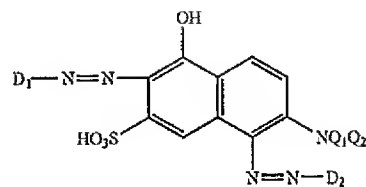
(b) Using a drop-on-demand inkjet head (bubble jet), the cotton satin pretreated according to Step (a) is printed with an aqueous ink containing

- 10% by weight of the reactive dye according to Example 21,
- 20% by weight of 1,2-propylene glycol and
- 70% by weight of water.

The print is dried completely and fixed in saturated steam for 8 minutes at 102° C., cold-rinsed, washed off at the boil, rinsed again and dried.

What is claimed is:

1. A reactive dye of formula



(1)

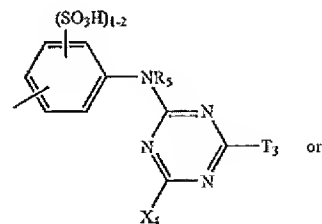
wherein

Q₁ and Q₂ are each independently of the other hydrogen or unsubstituted or substituted

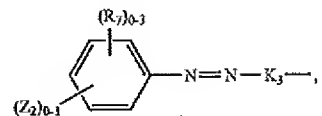
C₁-C₄ alkyl,

D₁ corresponds to a radical of formula (5) or (11)

(5)



(11)



wherein

R₅ is hydrogen or C₁-C₄ alkyl,

(R₇)₀₋₃ denotes from 0 to 3 identical or different substituents selected from the group halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, carboxy and sulfo,

X₄ is fluorine or chlorine,

Z₂ is a fibre-reactive radical of formula

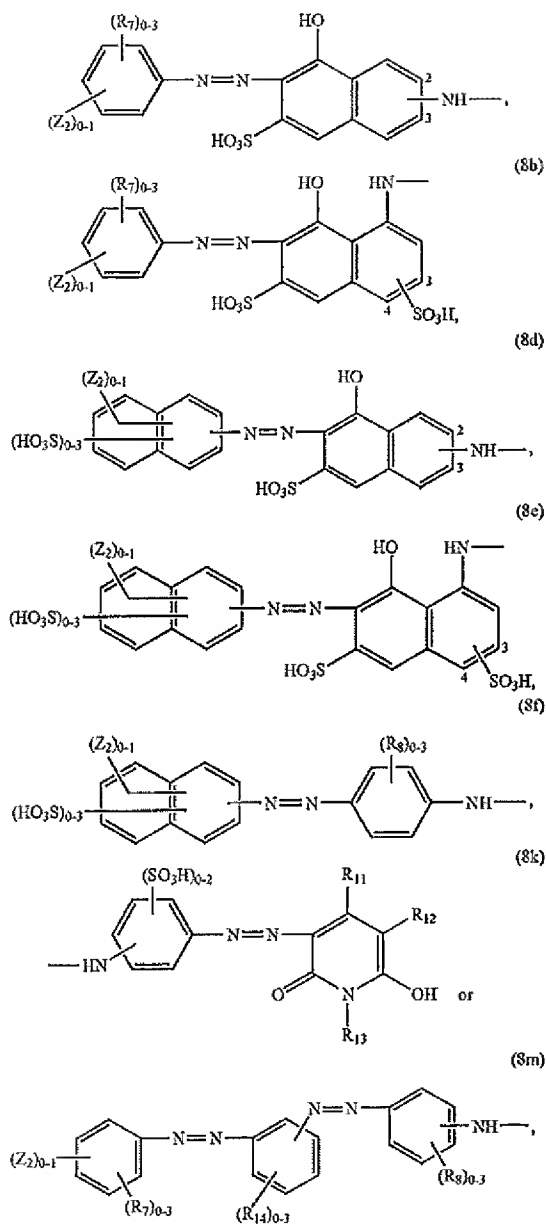


(3a),

wherein

Y is vinyl or β -sulfoethyl,

T₃ is a radical of formula



wherein

(R₇)₀₋₃ is as defined hereinabove,

(R₈)₀₋₃ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C₁-C₄ alkyl, C₁-C₄ alkoxy unsubstituted or substituted by hydroxy, sulfato or by C₁-C₄ alkoxy, amino, C₂-C₄ alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C₁-C₄ alkylsulfonylamino and sulfo,

R₁₁ and R₁₃ are each independently of the other hydrogen, C₁-C₄ alkyl or phenyl,

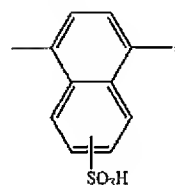
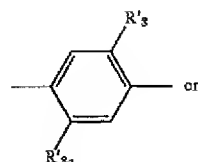
R₁₂ is hydrogen, cyano, carbamoyl or sulfomethyl,

(R₁₄)₀₋₃ denotes from 0 to 3 identical or different substituents from the group C₁-C₄ alkyl,

C₁-C₄ alkoxy, halogen, carboxy and sulfo, and

Z₂ is as defined hereinabove,

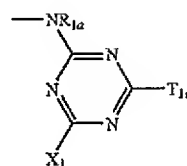
K₃ is the radical of a coupling component of formula



wherein

R'₈ is hydrogen, sulfo, or C₁-C₄ alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₂-C₄ alkanoylamino, ureido or a radical of formula



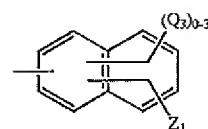
wherein

R_{1a} is hydrogen,

T₁ is amino; N-mono- or N,N-di-C₁-C₄ alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N-C₁-C₄ alkyl-N-phenylamino unsubstituted or substituted in the same way on the phenyl ring and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X₁ is chlorine

D₂ has the same definition as D₁ or is a radical of formula

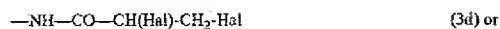
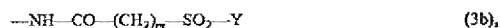


51

wherein

$(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, carboxy and sulfo and

Z_1 is a radical of formula



Y is vinyl or a $-\text{CH}_2-\text{CH}_2-\text{U}$ radical and U is a group that is removable under alkaline conditions,

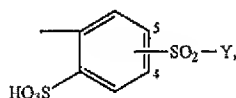
m and n are each independently of the other the number 2, 3 or 4, and Hal is halogen, with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

2. A reactive dye according to claim 1, wherein Q_1 and Q_2 are hydrogen.

3. A reactive dye according to claim 1, wherein

U is $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, $-\text{OSO}_3\text{H}$, $-\text{SSO}_3\text{H}$, $-\text{OCC}-\text{CH}_3$, $-\text{OPO}_3\text{H}_2$, $-\text{OCO}-\text{C}_6\text{H}_5$, $-\text{OSO}_2-\text{C}_1$ - C_4 alkyl or $-\text{OSO}_2-\text{N}(\text{C}_1$ - C_4 alkyl) $_2$.

4. A reactive dye according to claim 1 wherein D_2 is a radical of formula



wherein

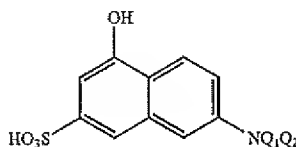
Y is vinyl or β -sulfatoethyl.

5. A process for the preparation of a dye of formula (1) according to claim 1, which comprises

(i) diazotisation of approximately one molar equivalent of an amine of formula



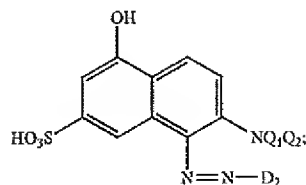
and reaction with approximately one molar equivalent of a compound of formula



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to form a compound of formula

(15a)



and

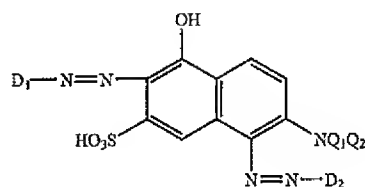
(ii) diazotisation of approximately one molar equivalent of an amine of formula



and reaction with approximately one molar equivalent of the compound of formula (15a) obtained according to (i) to form a compound of formula (1) according to claim 1 wherein D_1 , D_2 , Q_1 and Q_2 each have the definitions given in claim 1.

6. An aqueous ink that comprises a reactive dye of formula (1) according to claim 1.

7. A process for printing a substrate comprising spraying individual droplets of an aqueous ink onto the substrate from a nozzle in a controlled manner wherein the aqueous ink comprises a reactive dye of formula



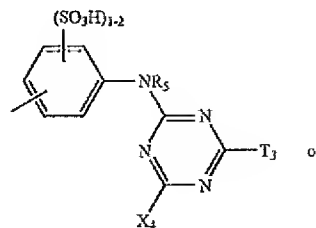
(1)

wherein

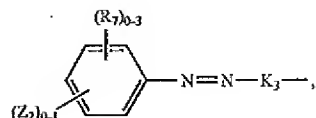
Q_1 and Q_2 are each independently of the other hydrogen or unsubstituted or substituted

C_1 - C_4 alkyl,

D_1 corresponds to a radical of formula (5) or (11)



(5)



(11)

wherein

R_5 is hydrogen or C_1 - C_4 alkyl,

$(R_7)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, carboxy and sulfo,

X_4 is fluorine or chlorine,

53

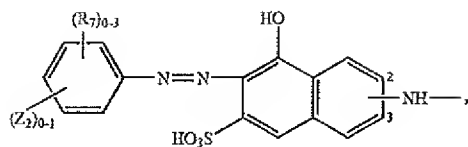
Z_2 is a fibre-reactive radical of formula



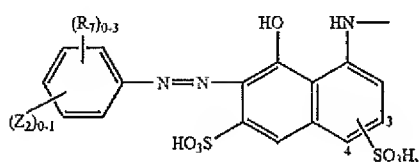
wherein

Y is vinyl or β -sulphatoethyl,

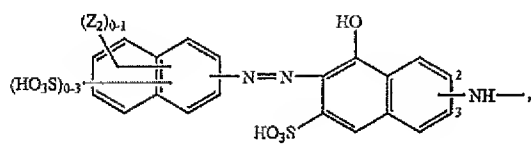
T_3 is a radical of formula



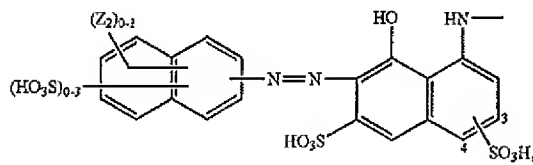
(8a)



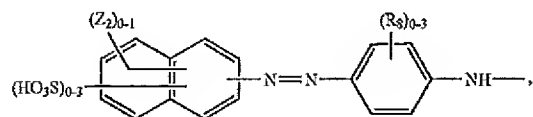
(8b)



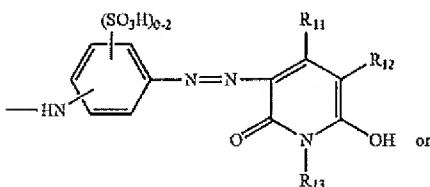
(8c)



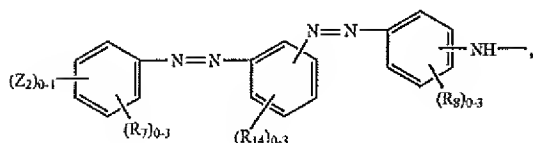
(8d)



(8e)



(8f)



(8g)

wherein

$(R_7)_{0-3}$ is as defined hereinabove,

$(R_8)_{0-3}$ denotes from 0 to 3 identical or different substituents from the group halogen, nitro, cyano, trifluoromethyl, sulfamoyl, carbamoyl, C_1 - C_4 alkyl, C_1 - C_4 alkoxy unsubstituted or substituted by hydroxy, sulfato or by

54

C_1 - C_4 alkoxy, amino, C_2 - C_4 alkanoylamino, ureido, hydroxy, carboxy, sulfomethyl, C_1 - C_4 alkylsulfonylamino and sulfo,

R_{11} and R_{13} are each independently of the other hydrogen, C_1 - C_4 alkyl or phenyl,

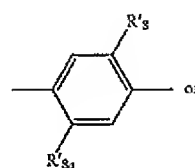
R_{12} is hydrogen, cyano, carbamoyl or sulfomethyl,

$(R_{14})_{0-3}$ denotes from 0 to 3 identical or different substituents from the group C_1 - C_4 alkyl,

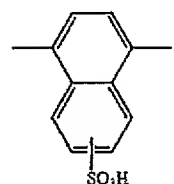
C_1 - C_4 alkoxy, halogen, carboxy and sulfo, and

Z_2 is as defined hereinabove,

K_3 is the radical of a coupling component of formula



(12a)

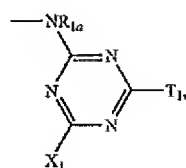


(12b)

wherein

R'_8 is hydrogen, sulfo, or C_1 - C_4 alkoxy unsubstituted or substituted in the alkyl moiety by hydroxy or by sulfato, and

R'_{8a} is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoylamino, ureido or a radical of formula



(3f)

wherein

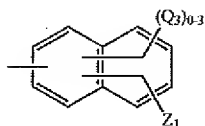
R_{1a} is hydrogen,

T_1 is amino; N-mono- or N,N-di- C_1 - C_4 alkylamino unsubstituted or substituted in the alkyl moiety/moieties by hydroxy, sulfato or by sulfo; morpholino; phenylamino unsubstituted or substituted on the phenyl ring by sulfo, carboxy, acetylamino, chlorine, methyl or by methoxy; or N- C_1 - C_4 alkyl-N-phenylamino unsubstituted or substituted in the same way on the phenyl ring and in which the alkyl is unsubstituted or substituted by hydroxy, sulfo or by sulfato; or naphthylamino unsubstituted or substituted by from 1 to 3 sulfo groups, and

X_1 is chlorine

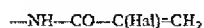
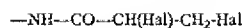
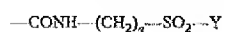
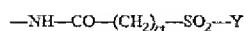
55

D_2 has the same definition as D_1 or is a radical of formula



wherein

$(Q_3)_{0-3}$ denotes from 0 to 3 identical or different substituents selected from the group halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, carboxy and sulfo and Z_1 is a radical of formula



(2)

5

56

Y is vinyl or a — CH_2 — CH_2 —U radical and U is a group that is removable under alkaline conditions, m and n are each independently of the other the number 2, 3 or 4, and

Hal is halogen

with the proviso that the dye of formula (1) does not contain a hydroxysulfonylmethyl group.

8. The process of claim 7 wherein the substrate is selected from textile fibre material, paper and plastic film.

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9. A method for dyeing fibre material which comprises applying a reactive dye of formula (1) according to claim 1 to the fibre material and fixing the reactive dye to the fibre material.

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10. The method according to claim 9 wherein the fibre material is a hydroxyl-group-containing fibre material or a nitrogen-group-containing fibre material.

(3a),

(3b),

(3c),

(3d) or

(3e),

11. The method of claim 9 wherein the fibre material is a cellulosic fibre material.

20

12. The method of claim 11 wherein the cellulosic fibre material is a cotton-containing fibre material.

* * * * *